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### The second-law efficiency of chemical processes\*

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**Abstract**—Equations are developed for calculating the thermodynamic efficiency of a chemical manufacturing process, using as a basis for the efficiency the second law, rather than a simple energy balance. This requires a consideration of the temperature at which heat is recovered, as well as the amount recovered and involves the use of the "availability" function, as developed by KEENAN. The thermodynamic efficiency of a typical ammonia oxidation process is shown to be about 6%, or is 11% when prescribed conditions of irreversibility are allowed for. By contrast the ordinary thermal efficiency, based on the first law, is as high as 32%.

**Résumé**—L'auteur développe des équations pour le calcul de l'efficacité thermodynamique d'un procédé de fabrication chimique en utilisant le second principe plutôt qu'un bilan thermique. Ceci nécessite la connaissance de la température à laquelle la chaleur est récupérée aussi bien que la quantité récupérée et implique l'utilisation de la fonction "disponibilité" développée par KEENAN.

L'efficacité thermodynamique d'une oxydation classique de l'ammoniac est d'environ 6% et de 11% quand il est tenu compte de l'irréversibilité. Au contraire, l'efficacité thermique basée sur le premier principe est de l'ordre de 32%.

#### 1. WASTE WORK

THE notion of the efficiency of a heat engine is a very familiar one; the second law sets a certain limit on the conversion of heat into work and the efficiency of any irreversible engine may be calculated relative to the reversible engine considered as a "target." The corresponding notion of the thermodynamic efficiency of a process for producing chemicals is much less familiar and this is the subject of the present paper. We shall be concerned with the target against which any actual process should be assessed, using as our basis the second law rather than a mere energy balance.

Let it be supposed that the temperature, pressure and composition of the raw materials have already been decided upon, and also the temperature, pressure and composition of the required product. The initial and final states of the process materials having been fixed in

this way, their changes of internal energy, entropy and volume are completely determined. These changes will be denoted  $\Delta U$ ,  $\Delta S$ , and  $\Delta V$  respectively.

As a measure of the efficiency of this process we can use *either* the minimum input of work, *or* the minimum input of heat from a source at a specified temperature. The former is the more convenient and we shall therefore use as our criterion the least amount of mechanical energy which must be supplied when, at the conclusion of the process, the only systems which have undergone any change are the process materials and the medium†. By the latter is meant the atmosphere and the earth's surface, (or cooling water at the temperature of the earth).

That is to say, the efficiency is to be computed on the basis that, at the end of the process, all auxiliary heat reservoirs, such as quantities

\*Based on two lectures given in the Chemical Engineering Department of the University of Minnesota in 1953.

†And, of course, the position of the "weight" which measures the performance of the mechanical energy.

of steam, have been restored to their original states, i.e. the medium is to be taken as the only source or sink. This is clearly the only sound basis, since the medium is the only heat reservoir available to man which does not require, for its maintenance, the using up of some of his resources.

In a considerable number of chemical processes it is possible, at least in principle, to obtain an output of useful energy. In such cases the corresponding criterion is the *maximum* amount of mechanical or electrical energy which could have been obtained from the specified process, when the only other body which undergoes any change is the medium. Of course, in the special case where the initial and final states of the process materials are at the same temperature and pressure as the atmosphere, the minimum work which must be applied is equal to the increase of their Gibbs free energy. (Or the maximum work which might be obtained is equal to the decrease). But in cases where the temperatures and pressures are not the same as those of the atmosphere the minimum work will be shown to be equal to the increase in "availability" of these materials.

The thermodynamic function known as the availability was developed by KEENAN [1] on the basis of some work of WILLARD GIBBS [2], but has not been applied at all extensively to chemical processes. The significance of this function for the present purposes will now be outlined.

Consider first of all the process as it is actually carried out. The first law may be written

$$\Delta U = q - w',$$

where  $\Delta U$  is the increase in internal energy of a fixed quantity of process materials passing through the chemical plant,  $w'$  is the work done by these materials and  $q$  is the heat they take in. For the present purposes it is convenient to write this equation in more detail and to change the sign of the work because most real processes require a positive input [e.g. to pumps].

Thus

$$\Delta U = -q_0 + \sum q_i - P_0 \Delta V + w, \quad (1)$$

where

$q_0$  is the heat given to the medium;

$\sum q_i$  is the sum of all other heat effects (e.g. from various supplies of steam), taken as positive for heat taken in by the process materials;

$P_0 \Delta V$  is the work done in displacing the atmosphere at its constant pressure  $P_0$ ;

$w$  is the total of all other items of work, taken as positive for work done on the process materials.

This equation will apply whether the process is batchwise or continuous, provided that  $w$  is taken to include the work required to cause inflow and outflow and is not merely the shaft work within the process itself. (Otherwise  $\Delta U$  would be replaced by  $\Delta H$  in the case of steady flow.

According to the second law the sum of all entropy changes caused by the process can only be positive or zero. Thus

$$\Delta S + \Delta S_0 + \sum \Delta S_i \geq 0,$$

where  $\Delta S$  is the entropy change of the process materials;

$\Delta S_0$  is the entropy change of the medium;

$\sum \Delta S_i$  is the sum of the entropy changes of the reservoirs which provide the heat effects  $q_i$ .

Alternatively it is convenient to define a quantity  $\sigma$  by means of the identity

$$\Delta S + \Delta S_0 + \sum \Delta S_i \equiv \sigma, \quad (2)$$

so that  $\sigma$  means literally the created entropy. Then according to the second law

$$\sigma \geq 0. \quad (3)$$

This device of writing a symbol for the amount by which the entropy of the universe has increased, as a result of the process, was first used at all extensively by the Belgian physicist DE DONDER. It introduces nothing which is not already contained in the second law but it does assist in making problems of irreversibility more easy to survey.

Now the medium acts merely as a heat reservoir at constant temperature  $T_0$  (which is in the region 280-300°K). Hence

$$\Delta S_0 = q_0/T_0$$

and therefore (2) may be written

$$\Delta S + \frac{q_0}{T_0} + \sum \Delta S_i = \sigma \quad (4)$$

Eliminating  $q_0$  between equation (1) and (4) we obtain

$$\Delta S + \frac{1}{T_0} (-\Delta U + \sum q_i + w - P_0 \Delta V) + \sum \Delta S_i = \sigma$$

Multiplying through by  $T_0$  and rearranging

$$w + \sum (q_i + T_0 \Delta S_i) = T_0 \sigma + \Delta U + P_0 \Delta V - T_0 \Delta S \quad (5)$$

So much for the process as it is actually carried out. Consider now what would be the work requirement if no heat reservoir, other than the medium, were allowed to undergo any change. The terms  $q_i$  and  $\Delta S_i$  in equation (5) would therefore be zero. On the other hand, the last three terms on the right hand side of (5) will have precisely the same values as for the actual process, since the change in state of the process materials is taken as fixed. For the same amount of created entropy the total work input  $w_i$  of such a process would therefore be given by the right hand side of (5). Thus

$$w_i = T_0 \sigma + \Delta U + P_0 \Delta V - T_0 \Delta S \quad (6)$$

The quantity  $w + \sum (q_i + T_0 \Delta S_i)$  on the left hand side of (5), which is the same as  $w_i$  in (6), is therefore the total amount of work which would be needed for the given process, for a particular value of  $\sigma$ , the created entropy, when the only systems which undergo any change are the process materials and the medium. This may perhaps be seen more clearly by noting that, in the process as actually carried out,  $\sum (q_i + T_0 \Delta S_i)$  is the additional work needed to restore the various heat reservoirs to their original states, at the expense of the medium. For consider the restoration of heat  $dq_i$  to the  $i$ th reservoir, by use of a refrigeration cycle, using the medium as the source. The necessary work is given by the familiar Carnot expression:

$$\begin{aligned} & \frac{T_i - T_0}{T_i} dq_i \\ &= dq_i - T_0 \frac{dq_i}{T_i} \end{aligned}$$

where  $T_i$  is the momentary temperature of the reservoir. Thus the work needed to restore  $q_i$  to the reservoir is

$$\begin{aligned} & \int dq_i - T_0 \int \frac{dq_i}{T_i} \\ &= q_i + T_0 \Delta S_i \end{aligned}$$

(where the sign of  $\Delta S_i$  arises from the fact that  $\Delta S_i$  refers to the process of taking heat from the reservoir).

It follows that the quantity  $w + \sum (q_i + T_0 \Delta S_i)$ , which is denoted  $w_i$  in (6), may be referred to as the "total equivalent work requirement" of the process, for a given value of  $\sigma$ . Now according to the second law  $\sigma$  can only be positive or zero. Therefore the *least* work requirement of the process is given by

$$w_{i \min} = \Delta U + P_0 \Delta V - T_0 \Delta S, \quad (7)$$

and this occurs when the process is carried out reversibly.

Conversely if the signs of  $\Delta U$ ,  $\Delta V$ , and  $\Delta S$  are such the process is able to deliver mechanical work, then the above expression gives the negative of the maximum work which may be obtained, the only changes being in the process materials and in the medium.

Comparing equations (5) and (7) [or (6) and (7)] it is evident that the quantity  $T_0 \sigma$  is the additional quantity of work\* which is used in the actual process as compared to the ideal reversible process. Thus  $T_0 \sigma$  may be called the "wasted work" or "dissipated energy." It is identical with the quantity which KEENAN calls the "irreversibility" of the process. For the present purpose the term waste work is the more descriptive. One of the functions of the chemical engineer is to devise his process so that  $\sigma$  is as small as possible, consistent with not too large a capital expenditure on the plant.

The quantity on the right hand side of equation (7) has been called by KEENAN the increase in availability in the process in question. DODGE [3] has given it the symbol  $\Delta B$ ,

$$\Delta B \equiv \Delta U + P_0 \Delta V - T_0 \Delta S. \quad (8)$$

\*Or the additional quantity of heat, expressed as its work equivalent by use of the Carnot factor.

Of course, if the initial and final temperatures and pressures of the process materials were the same as those of the medium,  $\Delta B$  would be the same as  $\Delta G$ , the increase of Gibbs free energy and we should have the familiar result that the minimum work which is needed is equal to the increase of  $G$ . However the utility of the present equations is not limited to isothermal or isopiestic processes, (as is the case when the Gibbs free energy itself is used). The equations may be employed, for example, to calculate the minimum necessary input of work in cases where the reagents enter the plant at a temperature or pressure quite different from those of the outgoing products.

Whenever the product is a final product, in the sense that it is not to be used in some subsequent process, the most economic conditions, from a thermodynamic standpoint, are obtained by discharging this product at the same temperature and pressure as the medium. For if it were at a temperature  $T$  different from  $T_0$ , an output of work could be obtained by operating a heat engine between the product and the medium, using whichever is the hotter as the "source" and whichever is the cooler as the "sink." Similarly if the product were discharged at a pressure different from  $P_0$ , the pressure of the atmosphere, additional work could be obtained by operating an expansion engine.

To summarise, equations (5) or (6) may be written

$$w_i = T_0 \sigma + \Delta B \quad (9)$$

or in words

(total equivalent work requirement of process)  
= (wasted work) + (increase in availability of process materials).

This increase in availability,  $\Delta B$ , is entirely determined by the initial and final states of the materials, together with the temperature and pressure of the medium. However the engineer still retains the liberty to try to make  $\sigma$ , and therefore  $w_i$ , as small as possible. This requires a suitable choice of the path between the given initial and final states, i.e. the choice of the details of operation. Moreover it is evident that in processes for which  $\Delta B$  is negative it is

possible to obtain an output of work. That is to say  $w_i$  is negative if  $\Delta B$  is negative and if  $\sigma$  is small or zero\*.

It is evident that the smallness of  $T_0 \sigma$ , relative to  $\Delta B$ , is a measure of the efficiency of the process. However it is not intended to propose an actual definition of the efficiency, since it seems impossible to put forward a definition which is equally satisfactory for  $\Delta B$  positive or negative. In the example which is now to be discussed it will be clear enough how the efficiency is to be understood.

## 2. THE WASTE WORK OF AMMONIA OXIDATION

As an illustration of the preceding discussion it is instructive to consider the production of nitric acid from ammonia. This is a process for which  $\Delta B$  is negative and the process is capable of yielding a far larger output of useful work than is actually obtained.

It will be supposed that the ammonia is delivered to the process as a liquid at 20°C, under its vapour pressure of 8.5 atm. The other reagents are water and air, each at 15°C and 1 atm. The end product of the process is 60% (wt.) nitric acid, together with the unused components of the air, all of which are assumed to be at 25°C† and one atmosphere.

For simplicity it will be supposed that the chemical efficiency of the conversion of ammonia into nitric acid is 100%. That is to say, for the purpose of an analysis of the thermodynamic efficiency of the process we shall disregard the complicating effect of the chemical efficiency, which is usually rather less than 100%\*\*.

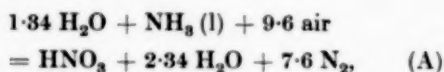
\*As a corollary, a spontaneous process within the medium is one in which there is a decrease of availability.

†The various temperatures are chosen as slightly different from each other in order to illustrate the method of calculation for cases where the differences are much larger.

\*\*The main chemical inefficiency is the conversion of about 5% of the ammonia into nitrogen, instead of into nitric oxide, on the platinum catalyst. Allowing for this would not appreciably alter the second law analysis of the process as given in this paper.



The overall chemical process may therefore be written



where the 1.34 moles of water on the left hand side of the equation is that which is required to give a 60% acid as the final product on the right hand side. The 7.6 moles of nitrogen on the right-hand side is, of course, that quantity of nitrogen which is incidental to the usage of 2 moles of oxygen in the reaction process.

Standard values at 25°C of the free energies and enthalpies of formation of the various compounds which occur in the above equation are available in the literature†. Using these data, together with the known partial pressures of H<sub>2</sub>O and HNO<sub>3</sub> above the 60% acid (in order to allow for their activity coefficients), it may be calculated that the following are the changes of the Gibbs free energy and enthalpy, when one gram mole of nitric acid, as a 60% solution, is formed at 25°C from air and from liquid ammonia, under its vapour pressure, at this temperature,

$$\Delta G_{298} = -74.2 \text{ kg cal}$$

$$\Delta H_{298} = -98.2 \text{ kg cal}$$

The volume change in this process is almost exactly that which corresponds to the disappearance of 2 moles of oxygen at 25°C and one atmosphere.

Hence

$$\Delta(PV)_{298} = -48.8 \text{ l atm.}$$

$$\equiv -1.2 \text{ kg cal}$$

Therefore

$$\Delta U_{298} = \Delta H - \Delta(PV)$$

$$= -97.0 \text{ kg cal}$$

$$\Delta S_{298} = (\Delta H - \Delta G)/T$$

$$= -0.0805 \text{ kg cal per } ^\circ\text{C.}$$

These are the changes in  $\Delta U$  and  $\Delta S$  which pertain to an isothermal process at 25°C. The actual process to be discussed was stated above to be one in which the products are at this temperature, whilst the liquid ammonia is

†The values used are from the National Bureau of Standards compilation, 1952.

under its vapour pressure at 20°C, and the air, together with the 1.34 moles of water needed to give the 60% acid, are at 15°C. To the above values of  $\Delta U$  and  $\Delta S$  we must therefore add the changes of  $U$  and  $S$  which are associated with the heating of liquid NH<sub>3</sub>, under its vapour pressure, from 20°C to 25°C and the heating of 9.6 moles of air and 1.34 moles of water from 15°C to 25°C.

When these small corrections are made, we finally obtain the following values for the changes of internal energy and entropy, between the assigned initial and final states of the process

$$\Delta U = -96.3 \text{ kg cal}$$

$$\Delta S = -0.0792 \text{ kg cal per } ^\circ\text{C.}$$

Also for the volume change

$$\Delta V = -41 \text{ l.}$$

Therefore the change of the availability is given by

$$\Delta B = \Delta U + P_0 \Delta V - T_0 \Delta S$$

$$= -96.3 - 1.0 + 22.8$$

$$= -74.5 \text{ kg cal,}$$

where  $P_0$  and  $T_0$  refer to the medium, and have been put equal to one atmosphere and 288°K respectively\*.

It follows that the process is capable of providing 74.5 kg cal of mechanical energy (for example as electrical power) per gram mole of nitric acid produced. This requires reversible conditions of operation, and a good approximation to this might be attained by carrying out the reaction electro-chemically, in a galvanic cell, if this were practicable.

Consider now the process as it is actually carried out, between the assigned initial and final states. Some typical figures, which refer to the customary process in which ammonia is oxidised on a platinum-rhodium catalyst, followed by absorption of the nitrogen oxides in packed

\*In this example the difference between  $\Delta G$  and  $\Delta B$  is seen to be very small. Much larger differences are to be expected in examples where the process materials enter or leave the system at temperatures appreciably different from  $T_0$ .

towers at atmospheric pressure, are as follows\*

input of electrical power	69 kwh per short ton $\text{HNO}_3$ .
steam recovery	0.8 tons per ton $\text{HNO}_3$ .

The second figure refers to the output of steam from a waste heat boiler which takes the hot gas from the ammonia oxidation. The steam in question is saturated at 50 lb. per square inch and is obtained from feed water at 20°C.

These figures may be re-expressed as follows

electrical power usage	4.1 kg. cal per g mole $\text{HNO}_3$
heat transferred to steam	31.9 kg cal per g mole $\text{HNO}_3$

Now it is to be noted that the energy which is recovered from the process, 31.9 kg cal, although quite substantial, is recovered as heat and not as work. If the local conditions at the factory are such that there is a requirement for heat (e.g. for space heating) this amount of energy could, in a sense, be allowed to count at its full value. However, when we are examining the absolute efficiency of the process, in the meaning of the second law, the fact remains that we could have obtained work from the process and actually we have only obtained heat – and work is always more valuable than heat on account of the Carnot conversion factor.

In fact the work equivalent of the recovered heat is the negative of the term  $(q_i + T_0 \Delta S_i)$  on the left hand side of equation (5)†. Here  $q_i$  has the value  $-31.9$  kg cal (negative since heat has been given to the steam in the process considered) and  $\Delta S_i$  is the increase of entropy in the process :

(feed water at 20°C)  $\rightarrow$  (saturated steam at 50 lb. per sq. inch).

Since there are  $0.8 \times 63 = 50.4$  grams of steam

\*These figures were kindly supplied by the Directorate of Ordnance Factories of the Ministry of Supply, but are entirely typical of ammonia oxidation as it is normally carried out.

†Note that there is only one such term in the process considered.

per gram mole of nitric acid, this entropy change is readily calculated from steam tables and, multiplying by  $T_0$ , we obtain  $T_0 \Delta S_i = 23.1$  kg cal. Therefore,

$$\begin{aligned} \text{work equivalent of recovered heat} &= \\ &= (-31.9 + 23.1) \\ &= -8.8 \text{ kg cal per mole } \text{HNO}_3. \end{aligned}$$

We now have all the terms occurring in equation (5) except  $T_0 \sigma$  and this is obtained by difference :

$$\begin{aligned} w + (q_i + T_0 \Delta S_i) &= T_0 \sigma + \Delta B \\ 4.1 - 8.8 &= T_0 \sigma - 74.5 \end{aligned}$$

Therefore  $T_0 \sigma$  has the value 69.8 kg cal per mole of  $\text{HNO}_3$ .

In brief there is a very large waste work or dissipation of energy in this particular process. The work equivalent of the recovered heat, less the input of electrical energy, is  $8.8 - 4.1 = 4.7$  kg cal; a perfectly reversible process would have yielded as much as 74.5 kg cal of useful work. The efficiency of the process, in the sense of the second law\*, might therefore be defined as the ratio of these two figures and is 6%.

### 3. PRESCRIBED DEGREE OF IRREVERSIBILITY

The efficiency of the process, as computed above, could be raised to 100% only if some means were available for carrying out the reaction under reversible conditions (for example in a galvanic cell using ammonia and oxygen electrodes). For this reason the efficiency of 6% may be called the absolute efficiency, since it is calculated relative to a standard of perfect reversibility.

On the other hand it is pertinent to ask the question : if, for practical reasons, it is prescribed that the reaction must be carried out in a certain way – namely by irreversible oxidation on platinum at 800-900°C – what is the efficiency with which the actual process is carried out, within the framework of this limitation ?

\*Not to be confused with the efficiency in the sense of the first law, as based on the energy balance. This would normally be defined as the ratio of the heat which is actually recovered to that which could have been recovered if there were no loss by convection and radiation to the atmosphere. This efficiency is 32% in the above example.

A similar situation exists in a great many industrial reactions and it is useful to calculate a practical efficiency, in addition to the absolute efficiency discussed above. The practical efficiency may be defined in such a way that it is unity (or 100%) when certain parts of the process are carried out under prescribed conditions of irreversibility, and all other parts are carried out under ideal reversible conditions.

As an example we shall consider once again the oxidation of ammonia to give 60% acid, the initial and final states being as described previously. The practical efficiency will be defined in such a way that it is 100% when the following conditions are satisfied.

- (a) All parts of the process are carried out reversibly except the chemical reactions and the mixing of the reagents.
- (b) The first reaction, the catalytic oxidation of ammonia, takes place at 850°C (1,123°K) and 1 atm. pressure and is carried out under completely irreversible conditions in the sense of performing no work (other than the displacement of the atmosphere). Similarly the second reaction, the absorption of the oxides of nitrogen, will be specified as taking place at 25°C and 1 atm. Under these conditions the heat evolved in the reactions is given by the change of a function of state and is  $-\Delta H^*$ .
- (c) The heat of reaction is recovered as mechanical work at the Carnot conversion factor (i.e. in a reversible engine).

\*It is important that the heat evolution in a reaction is determined by the change of a function of state of the process materials only when one or the other of the following conditions is satisfied. (a) The process is reversible and isothermal. In this case the heat evolution is  $-T \Delta S$  (and is not  $-\Delta H$ ). (b) The process is irreversible and the only work done is a displacement of the environment at constant pressure (a condition which prescribes the amount of work). In this case the heat evolved is again determined by the initial and final states and is  $-\Delta H$ . (c) The process is irreversible and takes place at constant volume (zero work). The heat evolved is  $-\Delta U$ .

The amount by which the practical efficiency is less than 100% is therefore a measure of the departure from reversibility of parts of the process other than the chemical reactions, e.g. the pumping of gases and acids, conversion of heat of reaction into useful work, etc.

The practical efficiency may be calculated by either of two methods—

- (1) A calculation is carried out on the amount of work which may be recovered from each part of the process, subject to the above conditions concerning irreversibility in the reactions.
- (2) Instead of calculating the recovery of work, we calculate how much is "wasted," i.e. the value of  $T_0 \sigma$  in the irreversible parts of the process.

Although the results are equivalent, an understanding of a given manufacturing process can best be attained if both methods are used. The first shows where to look for sources of recoverable energy, whilst the second emphasises the causes of wastage. Since  $\Delta B$  for the overall process is known, the two answers can be cross-checked and any discrepancy will indicate that some factor has been overlooked.

The first type of calculation is very familiar and therefore only the second will be discussed here. For this purpose it is first of all necessary to show how the entropy creation in a reaction may be calculated.

Consider any reaction taking place at constant temperature and pressure, the heat of reaction being transmitted to some other body (e.g. steam) which is at the same temperature. The created entropy is

$$\sigma = \Delta S + \Delta S_s,$$

where  $\Delta S$  and  $\Delta S_s$  refer to the entropy increases of the reaction system and the other body, respectively. If the only work done by the reaction system is due to its change of volume at constant pressure, then the heat transmitted to the other body is equal to  $-\Delta H$ , the decrease of enthalpy of the reaction system. The last equation may therefore be written

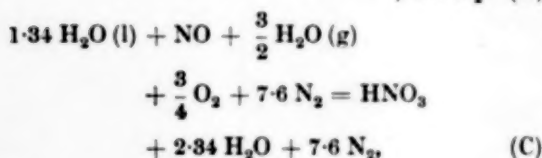
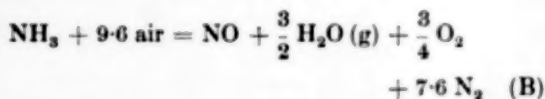
$$\begin{aligned}\sigma &= \Delta S - \frac{\Delta H}{T} \\ &= -\frac{\Delta G}{T},\end{aligned}\quad (10)$$

The entropy created in a chemical reaction\* taking place at constant temperature and pressure is therefore equal to  $-\Delta G$ , the decrease of Gibbs free energy of the reacting system, divided by the temperature  $T$  at which reaction takes place. The "wasted work," or "dissipated energy," or "irreversibility," of the process is therefore

$$T_0 \sigma = -\frac{T_0 \Delta G}{T} \quad (11)$$

#### 4. EXAMPLE ON AMMONIA OXIDATION

The overall reaction (A), as written in Section 2, must now be separated into its two component parts, which take place on the platinum catalyst, at 850°C and 1 atm, and in the absorption towers, at 25°C and 1 atm., respectively. These are†



where the 3/2 moles of gaseous water on the right hand side of (B) are formed in the oxidation reaction and the additional 1.34 moles of liquid water on the left hand side of (C) is the additional water which must be added to form the 60% acid.

From data in the literature on the free energy and enthalpy change in reaction (B) at 25°C, together with heat capacity data, it may be calculated that the value of  $\Delta G$  at 850°C (1,123°K)

\*For methods of calculating the entropy production in other types of natural process see the author's *Thermodynamics of the Steady State*, Methuen Monograph, 1951.

† The writing of the equation in this manner, which includes inert components such as nitrogen, assists in the calculation of the correct free energy charge, which includes a small term due to the free energy of mixing.

is about  $-78 \text{ kg cal/g mole NO}$ . Using equation (11) the waste work is therefore

$$\begin{aligned}T_0 \sigma &= \frac{288}{1123} \times 78 \\ &= 20 \text{ kg cal/g mole NO}.\end{aligned}$$

Similarly in reaction (C)

$$T_0 \sigma = \frac{288}{298} \times 12.7$$

as in equation below

$$= 12.3 \text{ kg cal/g mole HNO}_3.$$

Adding together the two items of waste work gives a total of 32.3 kg cal per mole of  $\text{HNO}_3$  and this is therefore the amount of energy which inevitably we fail to recover as useful work when the two reactions are carried out under the prescribed conditions of irreversibility.

If the whole process had been carried out reversibly it would have been possible to obtain 74.5 kg cal. of useful work, this being the value of  $-\Delta B$  for the overall process, as calculated previously. Therefore the maximum amount of mechanical energy which could possibly be obtained under the prescribed conditions is

$$74.5 - 32.3 = 42.2 \text{ kg cal/g mole HNO}_3$$

(as could also have been calculated by Method 1 on page 7).

According to the figures quoted in Section 2, the industrial process, as it is actually carried out, uses an input of 4.1 kg cal. of electrical energy (for pumping), whilst the recovered steam has a work equivalent of 8.8 kg cal. The net recovery is therefore

$$8.8 - 4.1 = 4.7 \text{ kg cal.}$$

The practical efficiency of the process may therefore be expressed by the fraction  $4.7/42.2$  or 11%.

This figure is considerably higher than the absolute efficiency of 6%, as calculated in Section 2, but is still very low. This is due to several factors.



- (a) The need for an input of 4.1 kg cal. of electrical energy, for the purpose of forcing the gases through the system and also for acid pumping. In brief there is an irreversibility due to fluid friction which could be avoided only by eliminating the pressure drop.
- (b) The incomplete recovery of the heat of reaction, the remainder being lost to the atmosphere and to the cooling water.
- (c) The fact that the steam is obtained at a temperature of only 138°C\* and not at the highest possible temperature of 850°C. The latter is feasible, in principle, in view of the fact that the ammonia oxidation takes place at this temperature.

This latter factor greatly reduces the work value of the steam, on account of the Carnot conversion factor as discussed previously.

Of course if the efficiency were computed on the basis that the steam is to be used for heating

purposes, the situation would appear considerably better. However this would be equivalent to computing the efficiency on the basis of the first law, rather than of the second.

In conclusion it is perhaps useful to summarize the main essentials for keeping entropy creation at a low level.

- (a) All heat transfers should take place at the least possible temperature difference.
- (b) Pressure drop and other forms of friction should be kept at a minimum.
- (c) Chemical reactions should be carried out under "resisted" conditions, so that they yield useful work.

The latter factor is certainly one of the most important in the chemical industry but unfortunately it is a matter of the greatest practical difficulty to carry out reactions under approximately reversible conditions. If some of the large-scale industrial reactions could be set up in the form of a fuel cell it would undoubtedly lead to a considerable saving of energy.

\*Saturated steam at 50lb. per square inch.

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## Volume changes on mixing in the cyclohexane-*n*-heptane-benzene system

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**Abstract**—It is well known that when petroleum fractions of different boiling range are mixed, their volumes are not strictly additive. However, little effort has been made to investigate the effect of composition, chemical nature of the components, and temperature on the magnitude and sign of the deviation from additivity. In order to obtain information on these factors, but to avoid the difficulties attendant with the interpretation of the data on such a complex mixture as petroleum, a study was made of the ternary system, cyclohexane-*n*-heptane-benzene. Volume changes on mixing were computed from the specific volumes of the pure compounds and their binary and ternary mixtures which were determined experimentally at 60°F and 100°F.

An increase in volume on mixing was noted in all mixtures studied, with the value of the maxima at 60°F ranging from about 0.30% in the case of a 60-40 mixture (by weight) of cyclohexane and *n*-heptane to 0.70% in the case of a 50-50 mixture of cyclohexane and benzene. In the ternary system a maximum of about 0.7% increase in volume was found in mixtures containing equal proportions of cyclohexane and benzene and up to 20 weight % *n*-heptane. The magnitude of the effect was reduced by an increase in temperature. It was found that the experimental results could be represented satisfactorily by equations based on the theory of regular solutions.

The data are of interest in connection with the manufacture of certain petroleum products that are prepared by the blending of different fractions.

**Résumé**—Dans un mélange de fractions de pétrole de points d'ébullition différents, le volume résultant n'obéit pas à la loi d'additivité. Quelques recherches, cependant, ont été faites pour étudier l'effet : de la composition, de la nature chimique des composants, de la température sur l'importance et le signe de l'écart à l'additivité. Pour obtenir des renseignements sur ces facteurs et dans le but d'éviter les difficultés inhérentes à l'interprétation des données sur un mélange aussi complexe que le pétrole, les auteurs ont étudié le système ternaire cyclohexane-*n*-heptane-benzène. Les variations de volume du mélange ont été estimées à partir des volumes spécifiques des constituants et des mélanges binaires et ternaires expérimentaux à 60 et 100°F.

Dans tous les mélanges étudiés, les auteurs ont remarqué une augmentation de volume maxima à 60°F et variant de 0.3% pour un mélange de 60-40 (en poids) de cyclohexane-*n*-heptane à 0.70% pour un mélange de 50-50 cyclohexane-benzène. Dans le système ternaire, l'augmentation de volume est de 0.7% dans des mélanges cyclohexane-benzène en égales proportions contenant jusqu'à 20% en poids de *n*-heptane. Un accroissement de température réduit l'importance de l'augmentation. Les résultats expérimentaux peuvent se représenter d'une manière satisfaisante par des équations basées sur la théorie des solutions réelles.

Toutes ces données présentent un intérêt pour la fabrication de certains produits pétroliers préparés par mélange de différentes fractions.

It is common knowledge that when two dissimilar liquids are mixed a change in volume and in temperature occurs. In general, the more dissimilar the compounds the larger will be the thermal and volumetric effects. In the blending of petroleum stocks, the similarity in the nature of the component hydrocarbons has led to the tacit assumption that the volume change due to mixing

is insignificant. While this may be true in the case of certain specific blends it is not generally true. THIELE and KAY [13] have shown that in the blending of a 50-50 mixture by weight, of light and heavy naphtha, a volume shrinkage of about 0.22% occurs. IOFFE [5] determined the change in volume on mixing in nine binary hydrocarbon systems and in five petroleum systems

each formed by blending various amounts of two different petroleum fractions. He reported volume changes amounting to as much as 1%, when the fractions blended, differed widely in their molecular weights and physical properties. CONNOLLY [2], in a study of the *n*-butane-benzene-cyclohexane systems, reported volume shrinkages in 50-50 mixtures of the *n*-butane-benzene and *n*-butane-cyclohexane binaries that varied from 0.4% at 60°F to 1.5% at 140°F. REEVES [7] and KURTZ and SANKIN [6], in summaries of the data on the volume change on mixing of hydrocarbon liquids reported in the literature, have presented additional evidence that volume changes on mixing in hydrocarbon systems can be appreciable and, in some blending operations, may affect the economic values assigned to individual products.

To obtain further information on the sign and the magnitude of the volume change on mixing in hydrocarbon systems, and on the factors affecting the change, a study of the ternary system cyclohexane-*n*-heptane-benzene was made. This system which is composed of compounds representative of the three general classes of hydrocarbons occurring in petroleum fractions, was chosen with the objective in mind of determining principally, the effect due to differences in the chemical nature of the components. Volume changes on mixing were computed from the specific volumes of the pure compounds and their binary and ternary mixtures which were determined in glass pycnometers at 60°F and 100°F. Equations for representing the relation between the percentage volume changes and the composition at constant temperature in binary and ternary mixtures were obtained by the application of the theory of regular solutions developed by HILDEBRAND [8] and SCATCHARD [9], [10], and the calculated values were compared with the experimentally derived values.

Volume changes in the binary system, cyclohexane-benzene have previously been determined by SCATCHARD, WOOD, and MOCHEL [11] at 80°C and later by WOOD and AUSTIN [14] from 15°C to 75°C at 10°C intervals. BROWN and EWALD [1] have obtained similar data for the *n*-heptane-benzene system at 25°C. KURTZ and SANKIN [6] have reported volume change for one mixture of

cyclohexane and *n*-heptane. So far as is known, ternary mixtures of cyclohexane, *n*-heptane, and benzene have not been studied before.

## EXPERIMENTAL

For the determination of the specific volume, three pycnometers were used so that simultaneous determinations on three samples could be carried out. Each of the pycnometers was constructed from a 50 ml pyrex volumetric flask provided with a ground glass stopper, by replacing a section of the neck with a short piece of 2 mm bore capillary. A ring was etched around the capillary at about its mid-section to serve as the mark defining the volume of the pycnometer.

The pycnometers were calibrated with freshly boiled, double-distilled water at 60°F and 100°F, using the values of the specific volume of water given in the International Critical Tables for these temperatures. Since the specific volume measurements and the calibrations were made at the same temperatures, no correction for the expansion of glass was necessary.

The weights of the empty and filled pycnometers as well as the weights of the pure compounds, which were mixed to make solutions of known composition, were determined with an analytical balance of 2 kg capacity with a sensitivity of 0.2 mg. The weights for use with the balance were checked against standard weights calibrated at the Bureau of Standards.

The specific volumes of the pure compounds and their binary mixtures were determined at the two temperatures using different samples. In the study of the ternary mixtures, the specific volumes were determined with one loading of the pycnometer by using two thermostated water baths. The procedure was to immerse the pycnometer first in the bath at 60°F until equilibrium was attained, then bring the liquid level to the reference mark, remove it and determine its weight; next, transfer it to the bath at 100°F and, after adjustment of the liquid level, remove it and redetermine its weight. The water baths were vigorously stirred and their temperatures maintained to within  $\pm 0.02^\circ\text{F}$  of the desired temperature.

## PREPARATION OF MIXTURES

The cyclohexane and *n*-heptane were purchased from the Phillips Petroleum Company and were guaranteed by the manufacturer to have a purity of 99 mole % or better; the benzene was Baker and Adamson's "reagent" grade. The three liquids were used without additional purification.

Binary mixtures of known composition were prepared by adding a quantity of each of the component liquids to a glass-stoppered bottle and weighing the bottle and contents after each addition of liquid. With the knowledge of the weight of the empty bottle, the weight of each of the liquids was then calculated and the composition expressed in terms of the weight fractions of the individual

components. It may be noted here that the weights of the components in the vapour phase were very small and the effect of neglecting them in the calculation of the weight fraction was negligible.

Ternary mixtures were made up in a similar manner by blending cyclohexane in various amounts with each of five binary mixtures of *n*-heptane and benzene of constant composition, prepared as stock solutions and designated by the symbols BH1 to BH5. Compositions were expressed in terms of the weight fractions of cyclohexane and stock solution.

Samples of these mixtures were transferred to the pycnometer by replacing the stopper of the stock bottle with a pressure siphon, similar to that used on a laboratory wash bottle. The end of the delivery tube of the siphon was drawn to a capillary so that it could be inserted through the capillary section of the pycnometer and the transfer made by applying air pressure over the liquid in the stock bottle. Changes in composition due to evaporation of the more volatile component during the transfer, were thus reduced to a minimum.

#### THEORETICAL CONSIDERATIONS

In the treatment of nonideal solutions, HILDEBRAND [3] has defined a "regular" solution as one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition. Such a solution is free of orienting and chemical effects so that the distribution and orientation of the molecules are random, just as in the ideal solution. Petroleum hydrocarbon mixtures may be considered as examples of regular solutions, since the compounds composing the mixtures are nonpolar and exhibit little, if any, solvation, association or chemical effects.

For a ternary regular solution at constant temperature, HILDEBRAND [4] gives the following equation for the change in volume on mixing of the components 1, 2, and 3:

$$\Delta V^M = \beta^\circ \Delta E_v^M \quad (1)$$

where:

$$\Delta E_v^M = V^\circ (A_{1,2} \phi_1 \phi_2 + A_{1,3} \phi_1 \phi_3 + A_{2,3} \phi_2 \phi_3) \quad (2)$$

$$\Delta V^M = V^M - V^\circ \quad (3)$$

$$\beta^\circ = \beta_1 \phi_1 + \beta_2 \phi_2 + \beta_3 \phi_3 \quad (4)$$

$$V^\circ = w_1 V_1 + w_2 V_2 + w_3 V_3 \quad (5)$$

$$\phi_1 = \frac{w_1 V_1}{V^\circ}; \phi_2 = \frac{w_2 V_2}{V^\circ}; \phi_3 = \frac{w_3 V_3}{V^\circ} \quad (6)$$

and  $w_1, w_2$  and  $w_3, V_1, V_2$ , and  $V_3, \beta_1, \beta_2$ , and  $\beta_3$  are weight fractions, specific volumes and isothermal compressibilities of the components 1, 2, and 3;  $A_{1,2}, A_{1,3}$ , and  $A_{2,3}$  are interaction constants for the respective binary pairs and  $V^M$  is the specific volume of the mixture. The per cent volume change then, is:

$$\Delta_{1,2,3} = \frac{100 \Delta V^M}{V^\circ} = 100 (\phi_1 \beta_2 + \phi_2 \beta_1 + \phi_3 \beta_3) (A_{1,2} \phi_1 \phi_2 + A_{1,3} \phi_1 \phi_3 + A_{2,3} \phi_2 \phi_3). \quad (7)$$

Use of this relation requires a knowledge of the compressibilities of the components as well as the interaction constants. However, by rearrangement, the equation can be put in such a form that the constants of the resulting equation can be determined in a simple manner from volume change data alone.

Equation (7) in expanded form is:

$$\begin{aligned} \Delta_{1,2,3} = & 100 A_{1,2} \phi_1 \phi_2 (\phi_1 \beta_1 + \phi_2 \beta_2 + \phi_3 \beta_3) \\ & + 100 A_{1,3} \phi_1 \phi_3 (\phi_1 \beta_1 + \phi_2 \beta_2 + \phi_3 \beta_3) \\ & + 100 A_{2,3} \phi_2 \phi_3 (\phi_1 \beta_1 + \phi_2 \beta_2 + \phi_3 \beta_3). \end{aligned} \quad (8)$$

Since  $\phi_1 + \phi_2 + \phi_3 = 1$ , it can be shown that,

$$\left. \begin{aligned} & 100 A_{1,2} \phi_1 \phi_2 (\phi_1 \beta_1 + \phi_2 \beta_2 + \phi_3 \beta_3) \\ & = \phi_1 \phi_2 \left[ 100 A_{1,2} \left( \frac{\beta_1 + \beta_2}{2} \right) \right. \\ & \quad \left. + 100 A_{1,2} \left( \frac{\beta_1 - \beta_2}{2} \right) (\phi_1 - \phi_2) \right] \\ & \quad \left. + \phi_1 \phi_2 \phi_3 \left[ \frac{100 A_{1,2}}{2} (2 \beta_3 - \beta_2 - \beta_1) \right] \right\} \quad (10) \end{aligned}$$

The second and third terms of equation (8) can be similarly rewritten. Adding the three terms together gives:

$$\left. \begin{aligned} \Delta_{1,2,3} = & \phi_1 \phi_2 [a_{1,2} + b_{1,2} (\phi_1 - \phi_2)] \\ & + \phi_1 \phi_3 [a_{1,3} + b_{1,3} (\phi_1 - \phi_3)] \\ & + \phi_2 \phi_3 [a_{2,3} + b_{2,3} (\phi_2 - \phi_3)] \\ & + c_{1,2,3} \phi_1 \phi_2 \phi_3 \end{aligned} \right\} \quad (11)$$

where, in terms of any components  $i, j$ , and  $k$

$$a_{i,j} = 100 A_{i,j} \frac{\beta_i + \beta_j}{2} \quad (12)$$

$$b_{i,j} = 100 A_{i,j} \frac{\beta_i - \beta_j}{2} \quad (13)$$



$$c_{i,j,k} = 100 A_{i,j} \frac{2\beta_k - \beta_j - \beta_i}{2} \quad (14)$$

and

$$c_{1,2,3} = c_{i,j,k} + c_{i,k,j} + c_{j,k,i} \quad (15)$$

For a binary system, on putting  $\phi_k = 0$ , equation (11) reduces to :

$$A_{i,j} = \phi_i \phi_j [a_{i,j} + b_{i,j}(\phi_i - \phi_j)] \quad (16)$$

Since  $a_{i,j}$  and  $b_{i,j}$  can be determined from measurements of volume change in the binary system composed of  $i$  and  $j$ , it follows that equation (11) expresses the percentage volume change on mixing three components in terms of the constants which can be derived from a study of the three binary systems with only the constant  $c_{1,2,3}$  to be obtained from the data on ternary mixtures.

Since the compressibilities of the components are of comparable magnitude, and furthermore, since the terms in "b" and "c" involve triple products of volume fractions, while the terms in "a" involve only double products of volume fractions, the contributions of the "b" terms and, particularly, the "c" term will be small in comparison to the contribution of the terms in "a." If the "c" term is dropped, then,

$$\Delta_{1,2,3} = \phi_1 \phi_2 \left[ a_{1,2} + b_{1,2}(\phi_1 - \phi_2) \right] + \phi_1 \phi_3 \left[ a_{1,3} + b_{1,3}(\phi_1 - \phi_3) \right] + \phi_2 \phi_3 \left[ a_{2,3} + b_{2,3}(\phi_2 - \phi_3) \right] \quad (11a)$$

and, to a high degree of approximation, the volume change in the ternary system can be expressed in terms of the volume changes in the binary systems.

In the investigation of the volume change on mixing in ternary mixtures, the volume change was determined by blending a mixture of constant composition of two of the components, say 2 and 3, with varying amounts of the third component. The measured volume change is then, the difference between the total volume change on mixing 1, 2, and 3 and the volume change on mixing 2 and 3.

Consider the mixing of  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  volumes of components 1, 2, and 3, where  $\phi_1 + \phi_2 + \phi_3 = 1$ , so that  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are also volume fractions in the ternary mixture. Let  $\Delta V_{2,3}$  be the volume

change and  $\Delta_{2,3}$  the per cent volume change on mixing  $\phi_2$  volumes of 2 with  $\phi_3$  volumes of 3;  $\Delta V_{1,2,3}$  the volume change and  $\Delta_{1,2,3}$  the per cent volume change on mixing  $\phi_1$  volumes of 1 with  $(\phi_2 + \phi_3 + \Delta V_{2,3})$  volumes of a mixture of 2 and 3, and  $\Delta V_{1,2,3}$  the volume change and  $\Delta_{1,2,3}$  the per cent volume change on mixing  $\phi_1$  volumes of 1,  $\phi_2$  volumes of 2 and  $\phi_3$  volumes of 3. Then :

$$\Delta_{1,2,3} = 100 \Delta V_{1,2,3} \quad (17)$$

$$= 100 (\Delta V_{2,3} + \Delta V_{1,2,3}) \quad (18)$$

$$= (\phi_2 + \phi_3) \Delta_{2,3} + (\phi_1 + \phi_2 + \phi_3 + \Delta V_{2,3}) \Delta_{1,2,3} \quad (19)$$

$$= (\phi_2 + \phi_3) \left( 1 + \frac{\Delta_{1,2,3}}{100} \right) \Delta_{2,3} + \Delta_{1,2,3} \quad (20)$$

$$= \Delta_{1,2,3} \left[ 1 + \frac{\Delta_{2,3}}{100} (\phi_2 + \phi_3) \right] + \Delta_{2,3} (\phi_2 + \phi_3) \quad (21)$$

Rearranging equation (21) gives :

$$\Delta_{1,2,3} = \frac{\Delta_{1,2,3} - \Delta_{2,3}(\phi_2 + \phi_3)}{1 + \frac{\Delta_{2,3}}{100}(\phi_2 + \phi_3)} \quad (22)$$

Neglecting the term,  $\frac{\Delta_{2,3}}{100}(\phi_2 + \phi_3)$  since it is much smaller than unity :

$$\Delta_{1,2,3} = \Delta_{1,2,3} - \Delta_{2,3}(\phi_2 + \phi_3) \quad (22a)$$

Equation (22), therefore, relates the per cent volume change in the second step of mixing with the per cent volume change in the first step (mixing 2 and 3) and in the overall process (mixing 1, 2, and 3). Substituting equations (11) and (16) into (22a) and considering the fact that volume fractions in equation (16) are to be based on the binary system, the following equation is obtained for  $\Delta_{1,2,3}$  :

$$\Delta_{1,2,3} = \phi_1 \phi_2 \left[ a_{1,2} + b_{1,2}(\phi_1 - \phi_2) \right] + \phi_1 \phi_3 \left[ a_{1,3} + b_{1,3}(\phi_1 - \phi_3) \right] + \phi_2 \phi_3 \left[ a_{2,3} + b_{2,3}(\phi_2 - \phi_3) \right] + c_{1,2,3} \phi_1 \phi_2 \phi_3 - (\phi_2 + \phi_3) \left[ \frac{\phi_2 \phi_3}{(\phi_2 + \phi_3)^2} \left\{ a_{2,3} + b_{2,3} \frac{(\phi_2 - \phi_3)}{(\phi_2 + \phi_3)} \right\} \right] \quad (23)$$

Equation (23) can be rearranged to give :

$$\Delta_{1,23} = \phi_1(\phi_2 + \phi_3)[a_{1,23} + b_{1,23}\{\phi_1 - (\phi_2 + \phi_3)\}] \quad (24)$$

where :

$$a_{1,23} = \frac{a_{1,2}}{1+K} + \frac{Ka_{1,3}}{1+K} - \frac{Ka_{2,3}}{(1+K)^2} + \frac{Kb_{2,3}}{(1+K)^2} - \frac{3Kb_{2,3}}{(1+K)^3} + \frac{Kc_{1,2,3}}{2(1+K)^2} \quad (25)$$

$$b_{1,23} = \frac{b_{1,2}}{1+K} + \frac{Kb_{1,3}}{1+K} + \frac{Kb_{2,3}}{(1+K)^3} - \frac{Kc_{1,2,3}}{2(1+K)^2} \quad (26)$$

and

$$K = \frac{\phi_3}{\phi_2} \quad (27)$$

The volume of the mixed components 2 and 3,  $\phi_{23}$ , is given by :

$$\phi_{23} = (\phi_2 + \phi_3) \left( 1 + \frac{\Delta_{2,3}}{100} \right) \quad (28)$$

The term  $\frac{\Delta_{2,3}}{100}$  may be neglected since it is much smaller than unity so that :

$$\phi_{23} = \phi_2 + \phi_3 \quad (28a)$$

Substituting equation (28a) into (24) gives :

$$\Delta_{1,23} = \phi_1\phi_{23}[a_{1,23} + b_{1,23}(\phi_1 - \phi_{23})] \quad (24a)$$

The resulting equation, therefore, is of the same form as equation (16) for a two-component system. By the same procedure the equation can be shown to apply to multicomponent systems of any complexity.

## RESULTS

For the computation of the volume change on mixing in the cyclohexane-*n*-heptane-benzene

Table 1. Volume Changes on Mixing in the Cyclohexane-*n*-Heptane, Cyclohexane-Benzene, and *n*-Heptane-Benzene Systems at 60°F

System	$W_i$	$V^M$	$(\Delta_{i,j})_e$	$(\Delta_{i,j})_e - (\Delta_{i,j})_e$	$\frac{(\Delta_{i,j})_e - (\Delta_{i,j})_e}{(\Delta_{i,j})_e} \times 100$
$i = C_6H_{12}$ $j = n-C_7H_{16}$	0.0	1.45425	—	—	—
	0.18134	1.42402	0.129	+ 0.005	+ 3.8
	0.35113	1.39528	0.224	0.000	0.0
	0.44672	1.37881	0.259	- 0.006	- 2.3
	0.63176	1.34634	0.284	- 0.009	- 3.2
	0.83535	1.30927	0.211	+ 0.005	+ 2.4
$i = C_6H_{12}$ $j = C_6H_6$	1.0	1.27739	—	—	—
	0.0	1.13220	—	—	—
	0.13886	1.15618	0.333	+ 0.007	+ 2.1
	0.28188	1.17952	0.547	- 0.012	- 2.2
	0.37588	1.19444	0.647	- 0.001	- 0.2
	0.50095	1.21317	0.684	- 0.009	- 1.3
$i = n-C_7H_{16}$ $j = C_6H_6$	0.69422	1.24038	0.599	+ 0.008	+ 1.3
	1.0	1.27739	—	—	—
	0.0	1.13220	—	—	—
	0.19903	1.20080	0.377	+ 0.009	+ 2.4
	0.39945	1.26726	0.508	- 0.012	- 2.4
	0.48893	1.29639	0.521	- 0.006	- 1.2
$i = C_6H_6$ $j = C_6H_6$	0.51361	1.30434	0.518	- 0.005	- 1.0
	0.56086	1.31949	0.506	- 0.002	- 0.4
	0.80535	1.39580	0.306	+ 0.005	+ 1.6
	1.0	1.45425	—	—	—
	0.0	1.13220	—	—	—
	0.19903	1.20080	0.377	+ 0.009	+ 2.4

system, the specific volumes of the 3 pure components, 5 mixtures of each of the 3 binary systems and 25 mixtures of the ternary system were determined at 60°F and 100°F. These data are given in Tables 1, 2, 3 and 4.

All of the data on the binary mixtures and the data on the ternary mixtures prepared by blending binary mixtures of constant composition of n-heptane and benzene with cyclohexane, were treated by application of the equations (16) and (24a) respectively. For this purpose both equations were rewritten in terms of volume change coefficient,  $\frac{100 \Delta V^M}{V^0 \phi_i \phi_j}$ , as :

$$\frac{100 \Delta V^M}{V^0 \phi_i \phi_j} = a_{i,j} + b_{i,j} (\phi_i - \phi_j) \quad (29)$$

where  $i$  is a pure component and  $j$  may be either a pure component or a binary mixture of constant

composition. Equation (29) may be put in the form :

$$\frac{100 \Delta V^M}{V^0 \phi_i \phi_j} = (m_{i,j} + n_{i,j}) \quad (30)$$

where

$$m_{i,j} = (a_{i,j} - b_{i,j}) \quad (31)$$

and

$$n_{i,j} = 2 b_{i,j} \quad (32)$$

By equation (30) it is evident that a plot of the volume change coefficient vs.  $\phi_i$  will result in a straight line with an intercept of  $m_{i,j}$  and a slope of  $n_{i,j}$  from which the values of  $a_{i,j}$  and  $b_{i,j}$  can be obtained. Figs. 1, 2, 3, and 4 show the experimental data plotted in this manner. Best straight lines were drawn through the points for a given system in order to evaluate the constants  $a_{i,j}$  and  $b_{i,j}$  which are listed in Table 5. Using these values and equations (16) and (24a)

Table 2. Volume Changes on Mixing in the Cyclohexane-n-Heptane, Cyclohexane-Benzene and n-Heptane-Benzene Systems at 100°F

System	$W_i$	$V^M$	$(\Delta_{i,j})_e$	$(\Delta_{i,j})_e - (\Delta_{i,j})_c$	$\frac{(\Delta_{i,j})_e - (\Delta_{i,j})_c}{(\Delta_{i,j})_e} \times 100$
$i = C_6H_{12}$ $j = n-C_7H_{16}$	0-0	1.49564	—	—	—
	0.17838	1.46442	0.073	- 0.004	- 5.5
	0.36396	1.43200	0.157	+ 0.007	+ 4.5
	0.47574	1.41206	0.180	- 0.002	- 1.1
	0.60884	1.38811	0.195	- 0.004	- 2.0
	0.78944	1.35495	0.166	0.000	0.0
	1.0	1.31458	—	—	—
$i = C_6H_{12}$ $j = C_6H_6$	0-0	1.16422	—	—	—
	0.23812	1.20544	0.451	+ 0.001	+ 0.2
	0.41788	1.23455	0.612	+ 0.001	+ 0.2
	0.51349	1.24932	0.637	+ 0.006	+ 0.9
	0.68186	1.27373	0.552	+ 0.002	+ 0.4
	0.85576	1.29691	0.311	- 0.002	+ 0.6
	1.0	1.31458	—	—	—
$i = n-C_7H_{16}$ $j = C_6H_6$	0-0	1.16422	—	—	—
	0.18079	1.22789	0.306	- 0.002	- 0.6
	0.35679	1.28827	0.451	- 0.003	- 0.6
	0.51125	1.34009	0.480	+ 0.008	+ 1.7
	0.66142	1.38912	0.410	+ 0.005	+ 1.2
	0.80390	1.43446	0.265	- 0.008	- 3.0
	1.0	1.49564	—	—	—

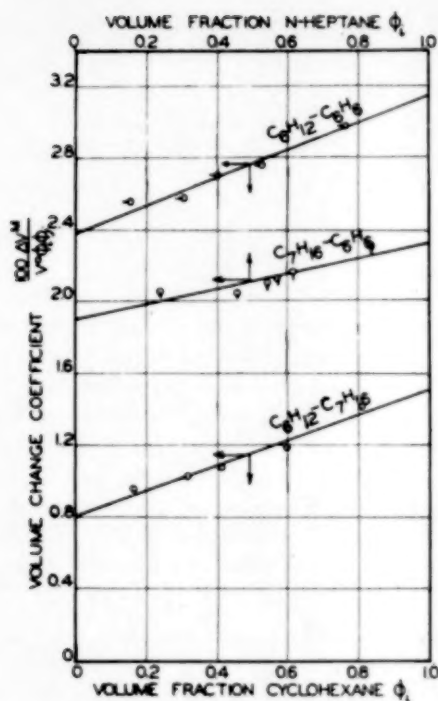


FIG. 1. Effect of composition on volume change coefficient for binary mixtures at 60°F.

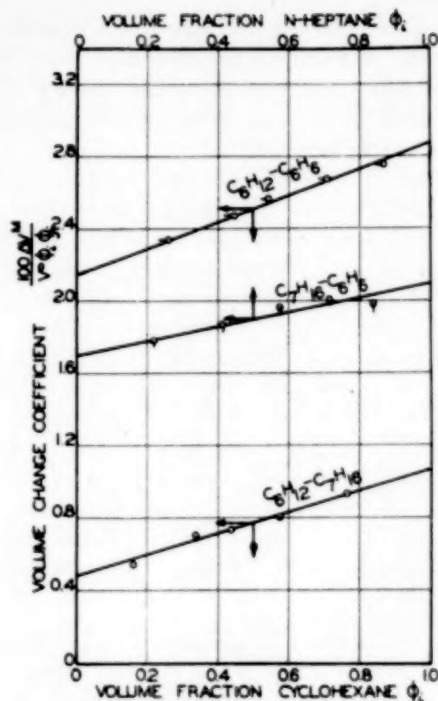


FIG. 2. Effect of composition on volume change coefficient for binary mixtures at 100°F.

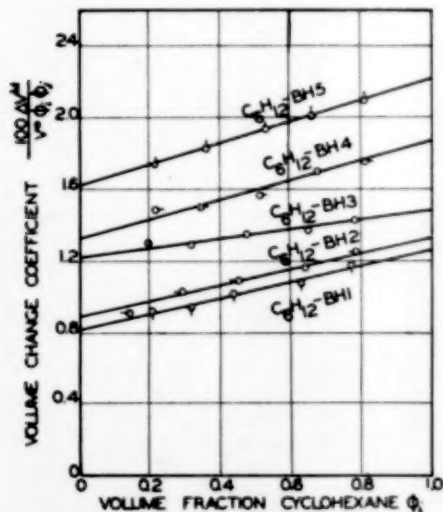


FIG. 3. Effect of composition on volume change coefficient for ternary mixtures at 60°F.

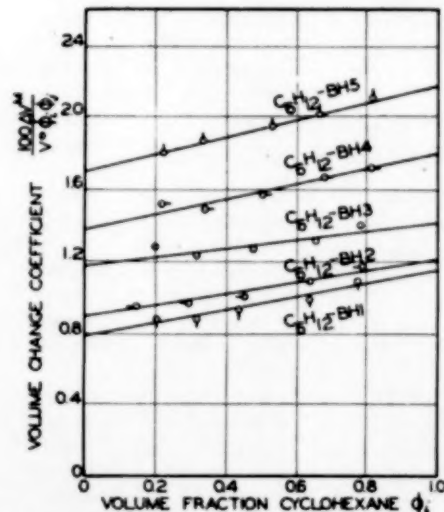


FIG. 4. Effect of composition on volume change coefficient for ternary mixtures at 100°F.



the curves of per cent volume increase vs. weight fraction, shown in Figs. 5, 6, 7, and 8 were calculated. The experimental values, represented by the circles, have been added for the sake of comparison. Values of  $a_{1,23}$  and  $b_{1,23}$  for the mixing of cyclohexane with stock solutions BH1 to BH5 were calculated by means of equations

(25) and (26) using the values of the constants listed in Table 5. These calculated values are compared with the experimental values obtained by equation (24a) in Table 6.

In order to obtain the volume changes on mixing the pure components cyclohexane, *n*-heptane and benzene, it was necessary to know the volume

Table 3. Volume Changes on Mixing Cyclohexane with Mixtures of *n*-Heptane and Benzene at 60°F

System	$W_i$	$v^M$	$(\Delta i, j)_e$	$(\Delta i, j)_e - (\Delta i, j)_c$	$\frac{(\Delta i, j)_e - (\Delta i, j)_c}{(\Delta i, j)_e} \times 100$
$i = C_6H_{12}$ $j = BH1$ $K = 0.1939$	0.0	1.39438	—	—	—
	0.21562	1.37147	0.148	+ 0.002	+ 1.4
	0.33153	1.35875	0.201	- 0.004	- 2.0
	0.45450	1.34513	0.249	+ 0.002	+ 0.8
	0.65202	1.32227	0.252	- 0.002	- 0.8
$i = C_6H_{12}$ $j = BH2$ $K = 0.4130$	0.78738	1.30597	0.206	+ 0.004	+ 1.9
	1.0	1.27868	—	—	—
	0.0	1.34883	—	—	—
	0.14614	1.34004	0.109	- 0.005	- 4.6
	0.30028	1.33059	0.212	+ 0.004	+ 1.9
$i = C_6H_{12}$ $j = BH3$ $K = 0.7768$	0.46105	1.32003	0.269	+ 0.001	+ 0.4
	0.65002	1.30668	0.265	- 0.004	- 1.5
	0.79518	1.29577	0.210	+ 0.004	+ 1.9
	1.0	1.27868	—	—	—
	0.0	1.30023	—	—	—
$i = C_6H_{12}$ $j = BH4$ $K = 1.4402$	0.19705	1.29863	0.204	+ 0.005	+ 2.4
	0.31687	1.29697	0.276	- 0.003	- 1.1
	0.47829	1.29423	0.334	0.000	0.0
	0.65214	1.29021	0.314	- 0.001	- 0.3
	0.78416	1.28644	0.242	0.000	0.0
$i = C_6H_{12}$ $j = BH5$ $K = 3.0899$	1.0	1.27868	—	—	—
	0.0	1.25152	—	—	—
	0.20849	1.26032	0.249	+ 0.008	+ 3.3
	0.33717	1.26493	0.337	- 0.004	- 1.2
	0.50135	1.27011	0.393	- 0.008	- 2.0
$i = C_6H_{12}$ $j = BH5$ $K = 3.0899$	0.67132	1.27450	0.374	+ 0.003	+ 0.8
	0.80673	1.27686	0.269	- 0.003	- 1.1
	1.0	1.27868	—	—	—
	0.0	1.20167	—	—	—
	0.20364	1.22091	0.292	- 0.002	- 0.7
$i = C_6H_{12}$ $j = BH5$ $K = 3.0899$	0.31676	1.23102	0.404	+ 0.003	+ 0.7
	0.51501	1.24731	0.482	0.000	0.0
	0.64664	1.25710	0.450	- 0.001	- 0.2
	0.79876	1.26728	0.324	- 0.001	- 0.3
	1.0	1.27868	—	—	—

changes occurring in the preparation of the stock solutions BH1, BH2, BH3, BH4, and BH5. From the specific volumes of the stock solution and the equation for the volume changes in the benzene-heptane system, established earlier, the exact compositions of these solutions were calculated. Hence, the per cent volume changes that occurred

in the preparation of the stock solutions as well as their ideal volumes could be calculated. Equation (21) was then applied to calculate the per cent volume change,  $\Delta_{1,2,3}$ , from the experimental data. The values are shown along with the compositions of the ternary mixtures in Tables 7 and 8.

Table 4. Volume Changes on Mixing Cyclohexane with Mixtures of n-Heptane and Benzene at 100°F

System	$W_i$	$V^M$	$(\Delta_{i,j})_e$	$(\Delta_{i,j})_e - (\Delta_{i,j})_e$	$\frac{(\Delta_{i,j})_e - (\Delta_{i,j})_e}{(\Delta_{i,j})_e} \times 100$
$i = C_6H_{12}$ $j = BH1$ $K = 0.1939$	0.0	1.43349	—	—	—
	0.21562	1.40968	0.141	+ 0.004	+ 2.9
	0.33153	1.39645	0.188	- 0.005	- 2.6
	0.45450	1.38225	0.227	- 0.004	- 1.7
	0.65202	1.35859	0.229	- 0.007	- 3.0
	0.78738	1.34186	0.192	+ 0.005	+ 2.7
	1.0	1.31385	—	—	—
$i = C_6H_{12}$ $j = BH2$ $K = 0.4130$	0.0	1.38637	—	—	—
	0.14614	1.37734	0.114	+ 0.002	+ 1.8
	0.30028	1.36732	0.199	- 0.003	- 1.5
	0.46105	1.35631	0.249	- 0.007	- 2.7
	0.65002	1.34259	0.250	- 0.003	- 1.2
	0.79518	1.33131	0.196	+ 0.004	+ 2.1
	1.0	1.31385	—	—	—
$i = C_6H_{12}$ $j = BH3$ $K = 0.7768$	0.0	1.33633	—	—	—
	0.19705	1.33456	0.200	+ 0.009	+ 4.7
	0.31687	1.33271	0.264	- 0.004	- 1.5
	0.47829	1.32975	0.315	- 0.006	- 1.9
	0.65214	1.32562	0.299	- 0.005	- 1.6
	0.78416	1.32186	0.239	+ 0.006	+ 2.6
	1.0	1.31385	—	—	—
$i = C_6H_{12}$ $j = BH4$ $K = 1.4402$	0.0	1.28616	—	—	—
	0.20849	1.29519	0.253	+ 0.009	+ 3.7
	0.33717	1.29981	0.334	- 0.007	- 2.1
	0.50135	1.30515	0.394	- 0.003	- 0.8
	0.67132	1.30952	0.366	+ 0.011	+ 3.1
	0.80673	1.31197	0.266	+ 0.002	+ 0.8
	1.0	1.31385	—	—	—
$i = C_6H_{12}$ $j = BH5$ $K = 3.0899$	0.0	1.23473	—	—	—
	0.20364	1.25464	0.304	+ 0.001	+ 0.3
	0.31676	1.26499	0.413	+ 0.002	+ 0.5
	0.51501	1.28170	0.487	0.000	0.0
	0.64664	1.29167	0.449	- 0.003	- 0.7
	0.79876	1.30216	0.326	+ 0.003	+ 0.9
	1.0	1.31385	—	—	—

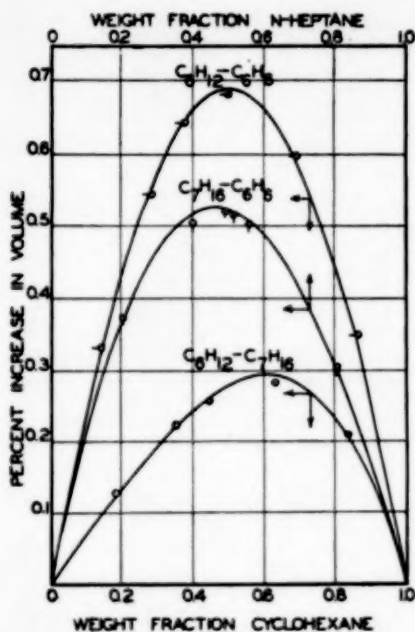


FIG. 5. Effect of composition on volume change in binary mixtures at 60°F.

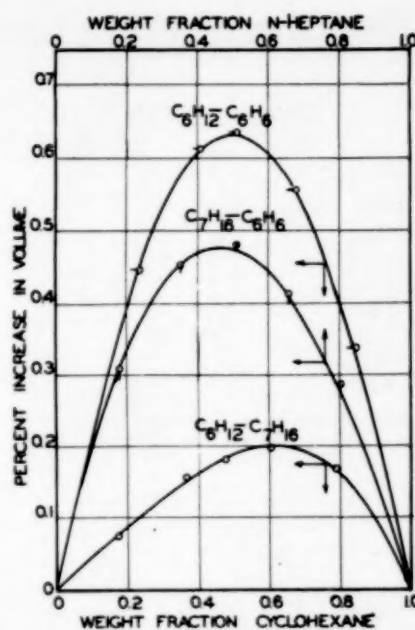


FIG. 6. Effect of composition on volume change in binary mixtures at 100°F.

$\Delta_{1,2,3}$  was also calculated by equation (11) and by the approximate equation (11a) using the constants  $a_{i,j}$ ,  $b_{i,j}$  and  $c_{1,2,3}$  given in Table 5.  $c_{1,2,3}$  was determined by the method of least squares from the difference between the values

of  $\Delta_{1,2,3}$  calculated by equation (21) and equation (11a). The resulting values of  $\Delta_{1,2,3}$  are given in Tables 7 and 8. By the use of a digital computing machine to solve equation (11) a series of points of constant per cent volume

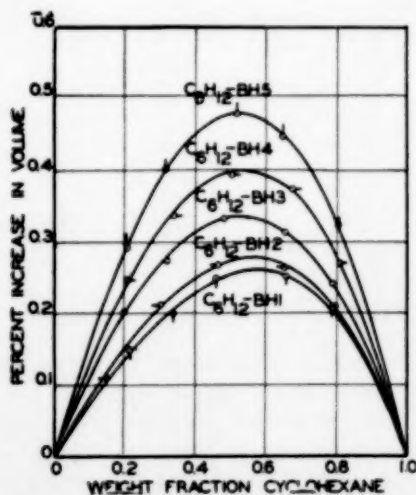


FIG. 7. Effect of composition on volume change in ternary mixtures at 60°F.

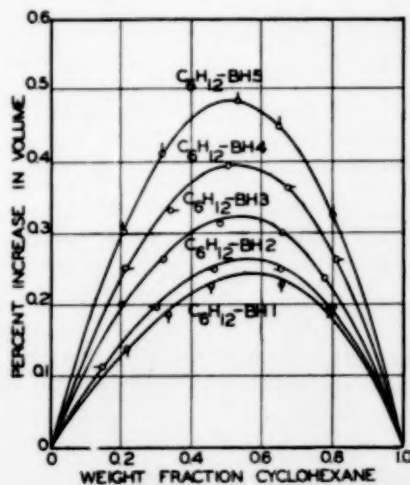


FIG. 8. Effect of composition on volume change in ternary mixtures at 100°F.

Table 5. Experimental Values of Constants of Equations (16) and (11) at 60°F and 100°F

System		60°F		100°F	
<i>i</i>	<i>j</i>	$a_{i,j}$	$b_{i,j}$	$a_{i,j}$	$b_{i,j}$
C <sub>6</sub> H <sub>12</sub>	<i>n</i> -C <sub>7</sub> H <sub>16</sub>	1.150	0.350	0.770	0.290
C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	2.760	0.380	2.510	0.360
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>6</sub>	2.110	0.210	1.900	0.200
C <sub>6</sub> H <sub>12</sub>	BH1	1.035	0.215	0.965	0.185
C <sub>6</sub> H <sub>12</sub>	BH2	1.105	0.215	1.050	0.160
C <sub>6</sub> H <sub>12</sub>	BH3	1.345	0.125	1.295	0.125
C <sub>6</sub> H <sub>12</sub>	BH4	1.600	0.270	1.585	0.215
C <sub>6</sub> H <sub>12</sub>	BH5	1.905	0.285	1.940	0.240

Values of  $C_{1,2,3}$  of Equation (11) are : - 1.00 at 60°F and + 1.40 at 100°F

Table 6. Comparison of Experimental and Calculated Interaction Constants for Mixing Cyclohexane with Mixtures of *n*-Heptane and Benzene at 60°F and 100°F

System		60°F		100°F	
		$a_{1,23}$	$b_{1,23}$	$a_{1,23}$	$b_{1,23}$
<i>i</i> = C <sub>6</sub> H <sub>12</sub>	Expt.	1.035	0.215	0.965	0.185
<i>j</i> = BH1	Calc.	1.013	0.447	0.848	0.229
<i>K</i> = 0.1939					
<i>i</i> = C <sub>6</sub> H <sub>12</sub>	Expt.	1.105	0.215	1.050	0.160
<i>j</i> = BH2	Calc.	1.082	0.493	0.985	0.194
<i>K</i> = 0.4130					
<i>i</i> = C <sub>6</sub> H <sub>12</sub>	Expt.	1.345	0.125	1.295	0.125
<i>j</i> = BH3	Calc.	1.176	0.515	1.202	0.176
<i>K</i> = 0.7768					
<i>i</i> = C <sub>6</sub> H <sub>12</sub>	Expt.	1.600	0.270	1.585	0.215
<i>j</i> = BH4	Calc.	1.457	0.510	1.500	0.182
<i>K</i> = 1.4402					
<i>i</i> = C <sub>6</sub> H <sub>12</sub>	Expt.	1.905	0.285	1.940	0.240
<i>j</i> = BH5	Calc.	1.895	0.474	1.873	0.223
<i>K</i> = 3.0899					

increase were computed for the ternary system. These data are shown graphically (by the curves) in Figs. 9 and 10.

#### PRECISION OF RESULTS

The experimental procedure was kept uniform as

far as possible so that the accuracy of the volume change data would be independent of any systematic errors in the individual specific volume measurements. The limits of precision of the various operations involved and the corresponding uncertainty in the specific volume measurements were estimated to be as follows :



Volume changes on mixing in the cyclohexane-*n*-heptane-benzene system

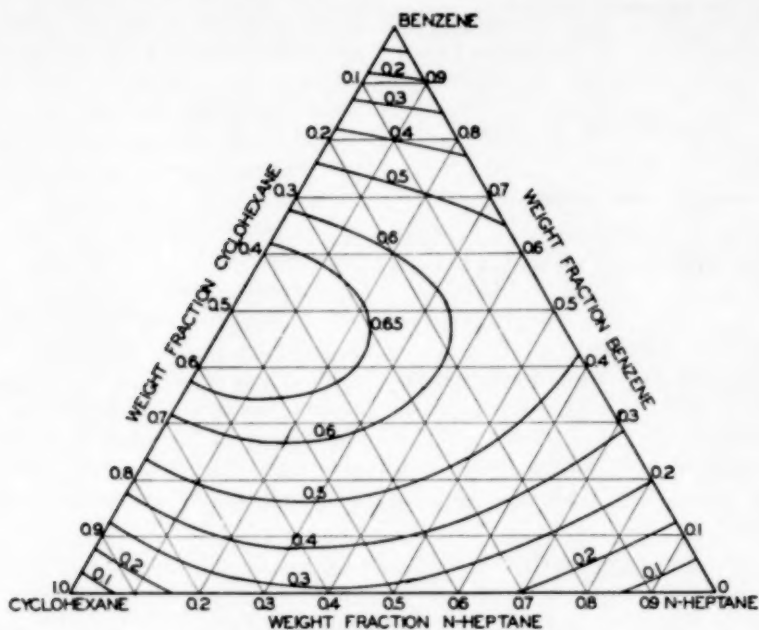


FIG. 9. Lines of constant per cent volume increase on mixing in the cyclohexane-*n*-heptane-benzene system at 60°F.

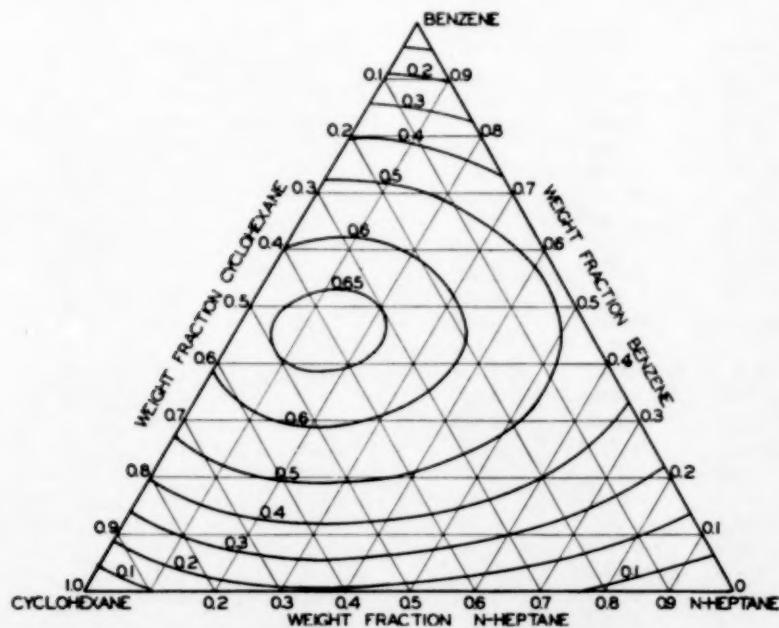


FIG. 10. Lines of constant per cent volume increase on mixing in the cyclohexane-*n*-heptane-benzene system at 100°F.

Operation	Precision	Uncertainty in Specific Volume parts per 100,000
Weighing	0.5 mg	1.2
Temperature	0.02 °F	2.0
Adjustment of liquid level in pycnometer	0.2 mm	0.8

Check determinations of the specific volume were found to be reproducible to within 8 parts in 100,000.

#### DISCUSSION

The relations between the composition and the per cent volume change on mixing in the cyclohexane-*n*-heptane-benzene system at 60°F and 100°F, are summarized in Figs. 9 and 10. It is to be noted that throughout the entire range of

composition an expansion in volume takes place on blending, with a maximum volume change of about 0.7% occurring somewhere in the region of a 45-10-45 cyclohexane-*n*-heptane-benzene mixture. Of the binary systems at 60°F, the cyclohexane-benzene system shows the greatest expansion with a maximum of about 0.7% and the cyclohexane-*n*-heptane the least with a maximum of 0.3% while the heptane-benzene system is intermediate with a maximum of about 0.54%. Increasing the temperature to 100°F reduces the values somewhat.

That the sign and the magnitude of these volume changes are to some extent associated with differences in the chemical nature of the components is substantiated by mixing data on these same compounds with other naphthenic, paraffinic

Table 7. Volume Changes on Mixing in the Cyclohexane-*n*-Heptane-Benzene System at 60°F

Composition weight fraction			$(\Delta_{1,2,3})_e$	$(\Delta_{1,2,3})_e - (\Delta_{1,2,3})_c$		$\frac{(\Delta_{1,2,3})_e - (\Delta_{1,2,3})_c}{(\Delta_{1,2,3})_e} \times 100$	
C <sub>6</sub> H <sub>12</sub>	<i>n</i> -C <sub>7</sub> H <sub>16</sub>	C <sub>6</sub> H <sub>6</sub>	Eqn. (21)	Eqn. (11a)	Eqn. (11)	Eqn. (11a)	Eqn. (11)
0.2156	0.6280	0.1564	0.398	-0.006	+0.011	-1.5	+2.8
0.3315	0.5352	0.1333	0.412	-0.019	+0.001	-4.6	+0.2
0.4545	0.4367	0.1088	0.423	-0.022	-0.003	-5.2	-0.7
0.6520	0.2786	0.0694	0.365	-0.033	-0.021	-9.0	-5.7
0.7874	0.1702	0.0424	0.273	-0.027	-0.021	-9.9	-7.7
0.1461	0.5579	0.2960	0.501	-0.013	+0.009	-2.6	+1.8
0.3008	0.4571	0.2426	0.536	-0.015	+0.015	-2.8	+2.8
0.4611	0.3521	0.1868	0.521	-0.027	+0.001	-5.2	+0.2
0.6500	0.2287	0.1213	0.430	-0.038	-0.021	-8.8	-4.9
0.7932	0.1338	0.0710	0.307	-0.025	-0.017	-8.1	-5.5
0.1970	0.4018	0.4012	0.629	+0.010	+0.041	+1.6	+6.5
0.3169	0.3418	0.3413	0.639	-0.004	+0.032	-0.6	+5.0
0.4783	0.2611	0.2606	0.612	-0.013	+0.019	-2.1	+3.1
0.6521	0.1741	0.1738	0.499	-0.026	-0.006	-5.2	-1.2
0.7842	0.1080	0.1078	0.357	-0.025	-0.016	-7.0	-4.5
0.2085	0.2777	0.5188	0.646	-0.006	+0.026	-0.9	+4.0
0.3372	0.2325	0.4808	0.669	-0.022	+0.014	-3.3	+2.1
0.5014	0.1748	0.3238	0.642	-0.028	+0.002	-4.4	+0.3
0.6718	0.1153	0.2134	0.537	-0.016	+0.001	-3.0	+0.2
0.8067	0.0678	0.1255	0.365	-0.016	-0.009	-4.4	-2.5
0.2036	0.1602	0.6362	0.585	-0.027	-0.003	-4.6	-0.5
0.3168	0.1375	0.5457	0.654	-0.031	-0.004	-4.7	-0.6
0.5150	0.0976	0.3874	0.657	-0.038	-0.017	-5.8	-2.6
0.6466	0.0711	0.2828	0.576	-0.035	-0.021	-6.1	-3.6
0.7988	0.0405	0.1607	0.395	-0.024	-0.019	-6.0	-4.8

and aromatic compounds reported in the literature. In a study of the effect of differences in chemical nature and physical properties of hydrocarbon compounds on their volume changes on mixing, IOFFE [5] found that, in general, when aromatic hydrocarbons are mixed with nonaromatic hydrocarbons an expansion occurs and that the expansion is greater with naphthenic than with paraffinic compounds. On the other hand, when paraffinic compounds are mixed with one another, volume contractions occur. KURTZ and SANKIN [6] and SCHIESSLER and co-workers [12] found that only small volume changes, frequently contractions, occur on mixing non-aromatic compounds whereas large volume expansions are obtained in mixtures containing aromatics. These observations are in agreement

with what has been found in this laboratory in the blending of petroleum distillates, namely that straight run Mid-Continent distillates (rich in paraffinic compounds) show contractions when blended with one another and expansions when blended with hydroformate distillates (rich in nonparaffinic compounds) [8].

In general, satisfactory agreement is obtained between the experimentally derived volume changes and the values calculated from the equations for regular solutions. Inspection of Tables 1, 2, 3, and 4, and Figs. 1 through 8 shows that the average deviation of the experimental per cent volume change for the binary systems from that calculated by equation (16) amounts to  $\pm 0.004$  units or 1.5%, which is of the same order of magnitude as the estimated experimental

Table 8. Volume Changes on Mixing in the Cyclohexane-*n*-Heptane-Benzene System at 100°F

Composition weight fraction			$(\Delta_{1,2,3})_e$	$(\Delta_{1,2,3})_e - (\Delta_{1,2,3})_c$		$\frac{(\Delta_{1,2,3})_e - (\Delta_{1,2,3})_c}{(\Delta_{1,2,3})_e} \times 100$	
$C_6H_{12}$	$n-C_7H_{16}$	$C_6H_6$	Eqn. (21)	Eqn. (11a)	Eqn. (11)	Eqn. (11a)	Eqn. (11)
0.2156	0.6280	0.1564	0.362	+ 0.036	+ 0.012	+ 10.0	+ 3.3
0.3315	0.5352	0.1333	0.378	+ 0.035	+ 0.007	+ 9.2	+ 1.9
0.4545	0.4867	0.1088	0.384	+ 0.037	+ 0.014	+ 9.6	+ 3.6
0.6520	0.2786	0.0694	0.331	+ 0.025	+ 0.009	+ 7.5	+ 2.7
0.7874	0.1702	0.0424	0.255	+ 0.024	+ 0.016	+ 9.4	+ 6.3
0.1461	0.5579	0.2960	0.467	+ 0.024	- 0.006	+ 5.1	- 1.3
0.3003	0.4571	0.2426	0.491	+ 0.031	- 0.012	+ 6.3	- 2.4
0.4611	0.3521	0.1868	0.476	+ 0.027	- 0.013	+ 5.7	- 2.7
0.6500	0.2287	0.1213	0.399	+ 0.021	- 0.003	+ 5.3	- 0.8
0.7952	0.1338	0.0710	0.283	+ 0.016	+ 0.005	+ 5.7	+ 1.8
0.1970	0.4018	0.4012	0.582	+ 0.046	+ 0.002	+ 7.9	+ 0.3
0.3169	0.3418	0.3413	0.589	+ 0.039	- 0.012	+ 6.6	- 2.0
0.4783	0.2611	0.2606	0.565	+ 0.037	- 0.008	+ 6.5	- 1.4
0.6521	0.1741	0.1738	0.466	+ 0.025	- 0.003	+ 5.4	- 0.6
0.7842	0.1080	0.1078	0.343	+ 0.023	+ 0.010	+ 6.7	+ 2.9
0.2085	0.2777	0.5138	0.609	+ 0.039	- 0.006	+ 6.4	- 1.0
0.3372	0.2325	0.4303	0.631	+ 0.030	- 0.020	+ 4.7	- 3.2
0.5014	0.1748	0.3238	0.616	+ 0.036	- 0.006	+ 5.8	- 1.0
0.6713	0.1153	0.2134	0.512	+ 0.035	+ 0.011	+ 6.8	+ 2.1
0.8067	0.0678	0.1255	0.351	+ 0.023	+ 0.013	+ 6.6	+ 3.7
0.2036	0.1602	0.6362	0.565	+ 0.023	- 0.011	+ 4.1	- 1.9
0.3168	0.1375	0.5457	0.636	+ 0.026	- 0.012	+ 4.1	- 1.9
0.5150	0.0976	0.3874	0.644	+ 0.030	0.000	+ 4.6	0.0
0.6466	0.0711	0.2823	0.562	+ 0.022	+ 0.002	+ 3.9	+ 0.4
0.7988	0.0405	0.1607	0.390	+ 0.019	+ 0.011	+ 4.9	+ 2.8

error. Table 6 shows that reasonably good agreement is obtained between experimental and calculated values of the constants  $a_{1,23}$  and  $b_{1,23}$  for mixing cyclohexane with constant composition mixtures of *n*-heptane and benzene. Tables 7 and 8 show that the approximate equation (11a), based on binary data alone, predicts the ternary volume changes to within about  $\pm 5\%$  of the experimental value. The use of a ternary interaction constant,  $c_{1,2,3}$ , brings the agreement to within  $\pm 2.5\%$ .

The per cent volume changes on mixing in the cyclohexane-benzene and *n*-heptane-benzene systems are in reasonably good agreement with the data reported on these systems in the literature. WOOD and AUSTIN [12] report per cent volume changes in a 50-50 mixture by weight of cyclohexane and benzene of 0.661 and 0.657 at 60°F and 100°F respectively, whereas 0.693 and 0.681 were found in this research. BROWN and EWALD [1] report a per cent volume change in a 50-50 mixture of *n*-heptane and benzene at 25°C (77°F) of 0.531 which may be compared to 0.526 at 60°F and 0.474 at 100°F reported here. KURTZ and SANKIN [6] report 0.27% volume change in *n*-heptane-cyclohexane mixture containing 53.2% *n*-heptane at an unspecified temperature while 0.287% volume change was obtained in the present study for the same composition at 60°F.

### CONCLUSIONS

It has been shown that the volume expansion that occurs when cyclohexane, *n*-heptane and benzene are mixed at room temperature, can be appreciable (0.7%) in certain concentration regions. It was shown also that the volume change on mixing benzene, an aromatic, with either cyclohexane, a naphthene, or *n*-heptane, a paraffin, is much larger than that on mixing cyclohexane with *n*-heptane. It is concluded that

this effect of the chemical nature of the components qualitatively explains the observation that volume expansions occur when distillates rich in aromatics are blended with non-aromatic distillates.

The equations for the per cent volume change on mixing in the binary and ternary systems of cyclohexane, *n*-heptane and benzene, based on the theory of regular solutions represent satisfactorily, the relation between the per cent volume change and the composition at constant temperature.

**Acknowledgements**—The authors wish to thank Dr. S. A. STERN, formerly of this laboratory, for his assistance and helpful suggestions in connection with the correlation of the data and Dr. J. F. CONNOLLY of the *Standard Oil Company of Indiana* for his interest and preliminary calculation of the constants of the equations.

### NOMENCLATURE

$A$  = interaction constant

$E$  = internal energy

$V$  = volume

$a, b, c, m,$  and  $n$  = constants

$K$  = ratio of volume fractions,  $\phi_3/\phi_2$

$w$  = weight fraction

$\beta$  = compressibility

$\phi$  = volume fraction

$\Delta$  = per cent volume change on mixing

$\Delta$  = increment (as a prefix)

### Subscripts

$c$  = calculated

$e$  = experimental

$i, j, k$  = any components

$v$  = constant volume process

1, 2, 3 = individual components (in specific case discussed, cyclohexane, *n*-heptane and benzene respectively)

### Superscripts

$M$  = property of a mixture

$^{\circ}$  = average property of the pure components

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## The separation of multicomponent mixtures of common gases by thermal diffusion

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**Abstract**—A brief résumé is given of theoretical and experimental work on the separation of binary and multicomponent mixtures of isotopes. The use of this information for the design of vertical hot-wire types of thermal diffusion columns is discussed. It is pointed out that no comparable experimental work exists for the separation of multicomponent common gases. The existing theory based on isotope separation is inadequate when dealing with common gases.

Experimental results are quoted for total reflux and continuous operation of a pilot-plant thermal diffusion column consisting of concentric tubes, and working on common gas mixtures. It is demonstrated from the results, that the separation of CO from H<sub>2</sub> may be enhanced by the introduction of CO<sub>2</sub> which produces a maximum separation of CO from H<sub>2</sub>. The possible reasons for the effect are discussed.

In conclusion, the absence of theory and the necessary complexity of such theory, when developed, indicates the necessity for a semi-empirical approach to the design of thermal diffusion columns for separation of multicomponent mixtures, based on pilot-plant information.

**Résumé**—Les auteurs donnent un rapide résumé d'un historique sur la séparation théorique et expérimentale des mélanges d'isotopes binaires ou à plusieurs constituants. Ils discutent l'usage de ces données pour l'étude des colonnes de diffusion thermique à fil chauffant vertical. Insistant sur le fait qu'il n'existe pas de guide pour la séparation de gaz usuels à plusieurs constituants, ils appliquent à ces gaz la théorie de la séparation des mélanges binaires d'isotopes.

Les auteurs citent les résultats expérimentaux obtenus avec une colonne pilote de diffusion thermique composée de tubes concentriques marchant en continu et à reflux total pour des mélanges de gaz usuels. Les résultats montrent que la séparation entre CO et H<sub>2</sub> peut être facilitée par l'introduction de CO<sub>2</sub>. Les causes possibles de cet effet sont discutées.

L'absence de théorie et la complexité obligatoire d'une telle théorie, quand elle est développée, montrent la nécessité d'opérer semi-empiriquement pour le calcul d'une colonne de diffusion thermique pour la séparation des mélanges multiples en se basant sur les données d'installations pilotes.

### INTRODUCTION

THE difficulty of solution of problems on the design of thermal diffusion apparatus from the separation of binary and/or multicomponent mixtures of common gases can be best understood by a review of the information available on isotope separation. The results of an experimental investigation on the separation of ternary mixtures of common gases in thermal diffusion pilot plant will then be discussed in the light of the review.

### *The theory of separation of binary mixtures of isotopes*

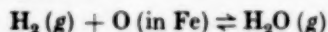
The classical theory is due to CHAPMAN [1] and ENSKOG [2]. Their treatment of the subject is extremely complex, and various other theories with a more elementary approach have been proposed by GILLESPIE [3], FRANKEL [4], and FÜRTH [5]. The theory of FRANKEL and JONES, developed by FÜRTH, has been extended by CACCIAPUOTI [6], FURRY [7], and FURRY and JONES [8].

A simple treatment has been given by WHALLEY and WINTER [9], essentially based on the work of FÜRTH. Their solutions are not exact, but have a value for first analysis. Theoretical values of the thermal diffusion coefficients  $k_T$  and  $\alpha$  were obtained by WINTER for mixtures  $H_2$ -He,  $H_2$ - $N_2$ ,  $H_2$ -Ne,  $N_2$ - $CO_2$ , and they showed that there was a marked temperature dependence of these coefficients not allowed for in the theory. Further, it was evident that the agreement between values of the coefficients calculated by exact and elementary theories depended on the binary mixture being considered, and in some cases lack of agreement was considerable.

*The theory of separation of multicomponent mixtures of isotopes*

The general theory for such separations has been given by HELLUND and UEHLING [10], but their equations are very complex and difficult of application. WHALLEY and WINTER [9] have extended their elementary approach used for binary mixtures, to the case of multicomponent systems, and in particular ternary mixtures of isotopes. They considered the effect of He on the separation of Ne isotopes, and also, the effect of Ne on the He isotopes. Their calculated values are not exact, but they indicate that the magnitude of the effect of the third gas is not large.

WINTER investigated the results of CHIPMAN and DASTUR [11], and first published experimental work on this subject. They introduced an inert gas into a steam-hydrogen mixture, and studied its effect on the apparent equilibrium constant of the system.



While WINTER accepted a qualitative agreement with his equation, he could not draw any quantitative conclusions from the work.

*The separation of multicomponent mixtures in vertical hot-wire type columns*

The first published work is that of ELDER [12]. It is a brief report of an experimental investigation on the separation of the neon isotopes with mass 20, 21, and 22 respectively. The apparatus consisted of a 2-stage 6 m long glass column of

hot-wire type, containing 3 litres of gas. Total reflux operation only was carried out, the concentrations at the end of the equilibrium period being recorded. The reported experimental operating data are inadequate to form an opinion as to the effect of any one component on the separation of the other two.

This work was extended by ELDER and McDONALD [13], the separation of the neon isotopes again being considered. The apparatus consisted of a 3 m glass tube of hot-wire type. The operating conditions were not well defined in the report. Compositions along the column were obtained at selected points by means of a mass spectrometer. On a plot of concentration versus height for each of the isotopes, it was found that the distribution of neon 21 along the column was not a smooth monotonic curve as for neon 20 and 22. This they attributed to a partial differential separation of neon 21 and 22, which is superimposed on the predominating separation of both of the heavier isotopes from 20. The result does not give a positive indication of the effect of the introduction of a third component on the separation of a binary mixture.

In 1953, CLUSIUS and SCHUMACHER [14] examined the problem of the separation of poly-mixtures of isotopes in CLUSIUS-DICKEL type columns. A comprehensive theoretical treatment based on CHAPMAN [1], JENSEN [15] and HELLUND [10], is given for binary mixtures, and poly-mixtures. An assumption is made that the enhancement of the separation produced by a vertical column is independent of the number of components present. This may be true as long as the density remains virtually independent of the concentration along the column, and would apply reasonably to isotope mixtures. It is assumed but not stated, that  $k_T$  and  $\alpha$  the thermal diffusion coefficients, are independent of concentration and temperature. SCHUMACHER claims that in mixtures of isotopes, the concentration of each component may be considered on its instantaneous value, and is not determined by other components. The solutions obtained are not exact, even for three component mixtures. A three component system is considered where a third component acts in such a way as to improve

the separation of the other two components over that separation which otherwise would be obtained. The choice of the third gas is based on a consideration of symmetry of the molecules, there being a maximum effect when the "Hilse-gasse" has a mass corresponding to the mean mass of the other two components. This gas would concentrate at some definite height in a column, and so would act as a buffer zone between the light and heavy ends, being easily separated from either. Krypton and xenon were separated in this way using silicon tetrafluoride as the third component. Extremely small withdrawal rates were used. The isotopes of argon were separated in continuous separation, but again long periods were allowed for equilibrium separation to be established. The theory was used to predict the size of apparatus required, but for krypton and xenon this could only be very approximate, and indeed it is doubtful whether the theory could be applied generally.

In conclusion, it is apparent that all existing theoretical and experimental work applies to either isotopes or cases where extremely small withdrawal rates are maintained. All the apparatus is of hot-wire type, with an extremely small tube. Such methods would be of little use for an industrial separation of common gases from multicomponent mixtures.

The difficulties inherent in the design of thermal diffusion columns for the separation of binary mixtures of common gases, have already been examined by the authors [16]. In 1953, work was carried out on a single thermal diffusion column of pilot plant dimensions. The experimental study was of a preliminary nature only, and was a logical development of the work carried

out in this apparatus on binary mixtures. The work is discussed below.

#### AN EXPERIMENTAL STUDY OF THE SEPARATION BY THERMAL DIFFUSION OF A THREE COMPONENT MIXTURE OF COMMON GASES

The gases chosen were  $H_2$ ,  $CO_2$ , and  $CO$ . The first experiments were to determine how the introduction of  $CO_2$  affected the separation of  $H_2$  from  $CO$ , and secondly, how  $CO$  affected the separation of  $H_2$  from  $CO_2$ .

The apparatus used and the operating techniques employed have already been described by the authors [16]. For the present experiments a 6 ft. column made in steel was used, comprising concentric cylinders. The dimensions of this column are given below. (This is column 2, described in the authors' paper ref. [16], where the inner tube is of stainless steel. This is not good practice due to enhancement of temperative asymmetry. However for column 2, it is felt that the effect is not so pronounced as to affect appreciably the results.)

The column was operated both under "total reflux", and "continuous" conditions. In the present case, the total reflux operation refers to the column closed at the lower end, but with circulation of gas in a closed circuit around the top of the column, a large gas holder being used to ensure a substantially constant top concentration. The continuous operation on the single column, refers to top circulation of gas, but with a continuous withdrawal of gas from the lower end of the column. Further, for common gases, this withdrawal rate is a substantial one as will be seen from the experimental figures.

EXPERIMENTAL RESULTS  
Table 1. Column dimensions, column 2.

Inner diameter of outer column	$3\frac{1}{8}$ "
Outer diameter of inner column	$1\frac{1}{8}$ "
Heated length	6 ft.
Annulus width	$\frac{1}{4}$ "
Mild steel outer tube. Stainless steel inner tube. Electrically heated element within the inner tube.	

Table 2. Total reflux column 2,  $T_h = 270^\circ\text{C}$ ,  $\Delta T = 250^\circ\text{C}$ ,  $2w = 1.80\text{ cm}$ , Introduction of  $\text{CO}_2$  into  $\text{H}_2/\text{CO}$  mixtures.

	$\text{CO}_2$	$\text{CO}$	$\text{H}_2$	$\text{H}_2/\text{CO}$	$P$	$\Delta c_e$
Initial gas	6.2	25.6	68.2	2.73	26.9	0
Equilibrium end concentration	12.0	51.0	37.0	0.74	57.5	30.6
Initial gas	15.0	19.0	66.0	3.37	23.0	0
Equilibrium end concentration	27.0	38.5	34.5	0.88	53.0	30.0
Initial gas	27.2	16.2	56.2	3.47	22.4	0
Equilibrium end concentration	38.0	28.0	35.0	1.20	44.5	23.9
Initial gas	43.0	12.0	45.0	3.75	21.1	0
Equilibrium end concentration	58.0	17.0	25.0	1.47	40.5	19.4
Initial gas	0.0	15.0	85.0	5.66	15.0	0
Equilibrium end concentration	0.0	29.1	70.9	2.44	29.1	14.1
Initial gas	0.0	22.0	78.0	3.54	22.0	0
Equilibrium end concentration	0.0	38.1	61.9	1.62	38.1	16.1

 $P$  = Percentage CO to a basis of  $\text{CO}_2$  free gas mixture.Table 3. Continuous operation, column 2.  $T_h = 270^\circ\text{C}$ ,  $\Delta T = 250^\circ\text{C}$ ,  $2w = 1.80\text{ cm}$ . Introduction of  $\text{CO}_2$  into  $\text{H}_2/\text{CO}$  mixtures.

	$\text{CO}_2$	$\text{CO}$	$\text{H}_2$	$\text{H}_2/\text{CO}$	$P$	$\Delta c$
Initial gas concentration	6.2	25.6	68.2	2.73	26.9	0.0
Final gas concentration at $\sigma = 480\text{ cc/min}$	10.0	40.7	49.3	1.24	44.6	17.7
$\sigma = 840\text{ cc/min}$	9.0	36.0	55.0	1.57	39.0	12.1
Initial gas concentration	15.0	19.0	66.0	3.37	23.0	0.0
Final gas concentration at $\sigma = 360\text{ cc/min}$	21.0	32.0	47.0	1.57	40.5	17.5
$\sigma = 670\text{ cc/min}$	19.6	29.0	51.4	1.77	36.1	13.1
$\sigma = 1,000\text{ cc/min}$	19.0	26.8	54.2	2.02	33.1	10.1
Initial gas concentration	27.2	16.2	56.2	3.47	22.4	0.0
Final gas concentration at $\sigma = 430\text{ cc/min}$	37.0	23.0	40.0	1.74	36.5	14.5
$\sigma = 860\text{ cc/min}$	34.4	20.6	45.0	2.18	31.4	9.0
Initial gas concentration	43.0	12.0	45.0	3.75	21.1	0.0
Final gas concentration at $\sigma = 76\text{ cc/min}$	50.6	15.5	33.9	2.20	31.4	10.3
$\sigma = 300\text{ cc/min}$	53.0	16.3	30.7	1.88	36.3	15.2

 $P$  = Percentage  $\text{CO}_2$  to a basis of CO free gas mixture;  $\sigma$  = withdrawal rate cc/min.

Table 4. Total reflux, column 2,  $T_h = 270^\circ\text{C}$ ,  $\Delta T = 250^\circ\text{C}$ ,  $2w = 1.80$  cms. Introduction of CO into  $\text{H}_2/\text{CO}_2$  mixtures.

	$\text{CO}_2$	CO	$\text{H}_2$	$\text{H}_2/\text{CO}_2$	$Q$	$\Delta c$
Initial gas concentration	18.0	20.8	61.2	3.4	22.8	0.0
Equilibrium end concentration	31.0	36.8	33.0	1.06	48.5	25.7
Initial gas concentration	29.6	2.2	69.0	2.38	29.6	0.0
Equilibrium end concentration	53.6	8.0	45.9	0.86	54.0	24.4
Initial gas concentration	26.0	7.4	66.6	2.56	28.1	0.0
Equilibrium end concentration	45.6	17.6	36.8	0.81	55.4	27.3
Initial gas concentration	22.0	0.0	78.0	3.54	22.0	0.0
Equilibrium end concentration	41.2	0.0	58.8	1.43	41.2	19.2

$Q$  = Percentage  $\text{CO}_2$  to a basis of CO free gas mixture.

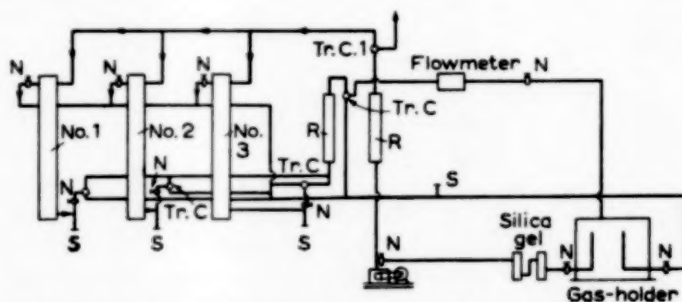


FIG. 1. Thermal diffusion pilot plant (detailed description Ref. [15]). N - needle valves; S - sample cocks; Tr.C - three-way cocks. (N.B. - Only Column 2 was used for the experiments on the separation of multicomponent mixtures.)

The system employed is represented in Fig. 1, and Fig. 2 describes the column. Gas analyses were obtained with a katharometer, and by Orsat analysis. The temperature of the inner tube was measured continuously, and also that of the cooling water. Care was taken to maintain a balanced operation. All experiments were conducted at atmospheric pressure.

In making up the gas mixtures in the gas holder at the beginning of a new set of experiments, it was difficult to predict the separation, and hence to reproduce the  $\text{H}_2/\text{CO}$  and  $\text{H}_2/\text{CO}_2$  ratios when steady-state conditions had been achieved. However they were obtained sufficiently closely to indicate any effects.

Gas rates were measured by a calibrated

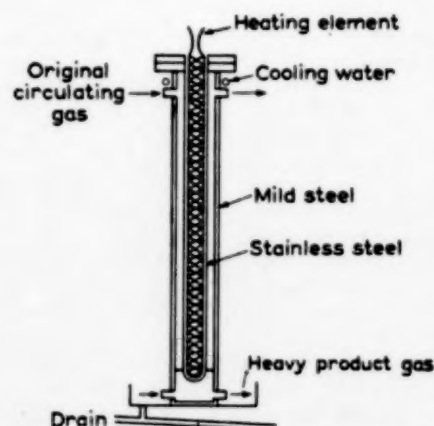


FIG. 2. 6 ft. column (No. 2). (Detailed description Ref. [15]).



rotameter on the top circulating gas, and by a direct bubble flowmeter on the withdrawn gas.

In the case of total reflux, equilibrium was established in one or two hours.

### DISCUSSION

An attempt has been made to predict the results obtained for the total reflux condition from the theory as developed by CLUSIUS and SCHUMACHER. This was not successful, and it would appear that equations based on the separation of isotopes do not apply to common gases.

The experiments on ternary mixtures of common gases recorded in this paper, appear to be the first carried out in pilot plant.

ELDER carried out experimental work with a ternary mixture of neon isotopes. Although he obtained an inflection in the Ne curve, the concentrations of the heavy component continued to increase down the column. This is also true of the separations carried out by CLUSIUS and SCHUMACHER. In the latter case, it was established that the third component of intermediate properties to the pair of isotopes being separated tended to concentrate somewhere intermediate between the top and bottom of the column.

No samples were taken along the tube in the present investigation, but it is doubtful if the third component, either CO or CO<sub>2</sub>, acts in a similar way in hydrogen. The molecules differ considerably from each other, and neither can be considered as being intermediate in properties between hydrogen and the other component. It would have been more accurate if the same initial concentration of the heavy component could have been used, but as will be seen from the H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> ratios, the deviation is not very large, and the result obtained based on the enrichment  $\epsilon$  is large enough to accept in principle.

It will be observed from Fig. 3 for total reflux operation, that when CO<sub>2</sub> is introduced into a H<sub>2</sub>/CO mixture, the enrichment of CO in H<sub>2</sub> at the bottom of the column, passed through a maximum. The initial concentration at the top of the column remains virtually unchanged by the use of a large gas holder in a closed circuit. At higher initial CO<sub>2</sub> concentrations, the enrich-

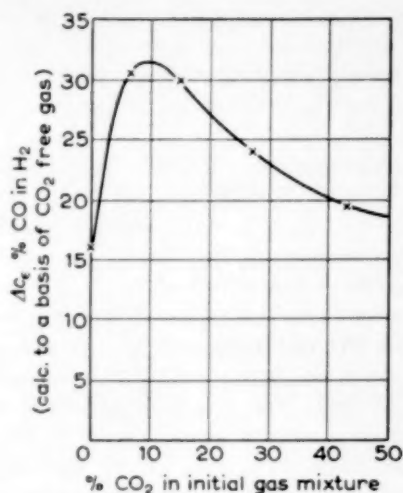


FIG. 3. Total reflux operation - 3-component mixture. Column 2:  $\Delta T = 250^\circ\text{C}$ ,  $2w = 1.80$  cm., H<sub>2</sub>/CO approx. constant.

ment of CO approaches a value one would expect for the binary mixture H<sub>2</sub>/CO. The CO<sub>2</sub> is itself concentrated at the bottom of the column.

The experiments were repeated under total reflux conditions with the introduction of CO into H<sub>2</sub>/CO<sub>2</sub> mixtures. (Fig. 4). The maximum was again recorded, with an initial CO concentration of 22.0% CO in the mixture. The curve

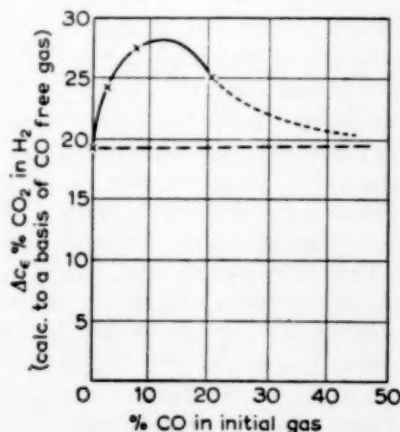


FIG. 4. Total reflux operation - 3-component mixture. Column 2:  $\Delta T = 250^\circ\text{C}$ ,  $2w = 1.80$  cms. H<sub>2</sub>/CO<sub>2</sub> of the same order of magnitude (2.56-3.54).

did not show such a rapid increase in  $\Delta c$ , i.e. improvement in the separation of  $\text{CO}_2$  from  $\text{H}_2$ . These results confirm the experimental values obtained for the introduction of  $\text{CO}_2$  into  $\text{H}_2/\text{CO}$  mixtures.

Consider the result obtained with 15%  $\text{CO}_2$  in the initial  $\text{CO}/\text{H}_2/\text{CO}_2$  mixture. Initial concentration of CO on the  $\text{CO}_2$  free gas is 23%. If the mixture were a binary of  $\text{H}_2/\text{CO}$ , this would give an end concentration of 29.1% CO, and an enrichment factor of 1.27. In the presence of  $\text{CO}_2$ , the CO end concentration, to a basis of  $\text{CO}_2$  free gas, becomes 53.0%, with an enrichment factor of 2.30. This is a considerable improvement.

In the same way, consider the separation of  $\text{CO}_2$  from  $\text{H}_2$ . In the absence of CO, the enrichment would be from 18.5%  $\text{CO}_2$  to an equilibrium value of 36.0% an enrichment factor of 1.58. In the presence of CO however, the end concentration to a basis of CO free gas becomes 43.8%, with an enrichment factor of 2.36. It is again apparent that the presence of CO enhances the separation of  $\text{CO}_2$  from  $\text{H}_2$  quite considerably.

It may be concluded from these results that any design would have to take into account the mutual effect of the molecules, and it cannot be accepted that the separation of  $\text{CO}_2/\text{H}_2$ ,  $\text{CO}/\text{CO}_2$ , and  $\text{CO}/\text{H}_2$  mixtures independently would be a guide to the behaviour of the three component mixture in the column. There is a large density change along the column, so that the premises used in theoretical work with isotopes would not hold for common gases.

The reasons for the results of these experiments on ternary mixtures, are a matter of conjecture in the absence of an exact theory for the separation of common gases either in binary or ternary mixtures. The effect may be due entirely to density and viscosity changes improving the operating characteristics of the column. This opinion would be quite acceptable for the improved separation of CO from  $\text{H}_2$  by the introduction of  $\text{CO}_2$ , as the heavier  $\text{CO}_2$  molecules improve the thermal syphoning, and the  $\text{CO}_2/\text{H}_2$  system has a better separation factor than  $\text{CO}/\text{H}_2$ . If however the molecules do not act independently, then it would not be surprising

if the greater ease of separation of  $\text{CO}_2$  from  $\text{H}_2$  would affect the  $\text{CO}/\text{H}_2$  separation. It does not however, and other reasons have to be found.

A reason which appears to be worthy of some consideration, is the possibility that 'sweep diffusion' is superimposed on the thermal diffusion effect. In this way three processes would have to be considered in the design of a Clusius type column, (i) thermal diffusion, (ii) natural diffusion, (iii) sweep diffusion. Sweep diffusion is discussed by CICHELLI, WEATHERFORD and BOWMAN [17] and is itself a method for the separation of gases. In this method a readily condensable gas or vapour is introduced into a binary mixture. This vapour moves towards a cooled surface where it is condensed and removed from the system. The movement of the vapour has a drag effect on the molecules, the effect being different for the components being separated. The component having the lower natural diffusion rate through the vapour is "swept" out of the mixture.

In the present experiments, it could be considered that the  $\text{CO}_2$  being separated more easily from  $\text{H}_2$  than the CO, moves rapidly to the cold wall, where it is removed from the separating zone by the syphon action of the column. In this way, superimposed on the movement of the CO molecules to the cold wall, is a sweep action. The CO will have a lower coefficient of natural diffusion through the  $\text{CO}_2$  than through  $\text{H}_2$ , so that back-diffusion of CO will be reduced and an enhanced separation is obtained over that obtainable by thermal diffusion alone. This would also explain why the effect is greater for the introduction of  $\text{CO}_2$  into  $\text{H}_2/\text{CO}$  mixtures, than for CO in  $\text{H}_2/\text{CO}_2$  mixtures. The theoretical analysis would be extremely complex, but the optimum concentration of the heaviest component could be found as above from pilot plant study.

In the same apparatus results were obtained for the effect of withdrawal rate, in continuous operation, on the separation of  $\text{H}_2/\text{CO}/\text{CO}_2$  mixtures. The results are given in Table 3, and Fig. 5. Under steady conditions of operation, the separation is impaired by an increase in withdrawal rate. This is shown in Fig. 5, each curve representing a different gas mixture. The curves

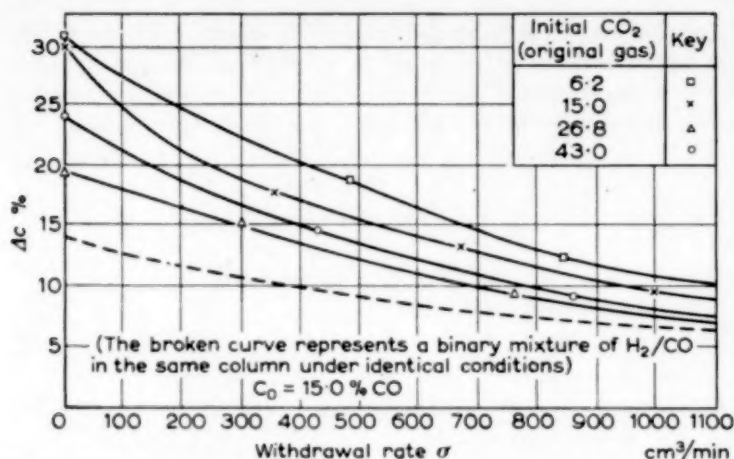


Fig. 5. Continuous operation - 3-component mixture. Column 2:  $\Delta T = 250^\circ\text{C}$ ,  $2v = 1.80$  cms.

intersect the ordinate at the total reflux value of the concentration. On the same graph is plotted the experimental curve obtained with a binary mixture of H<sub>2</sub>/CO with initial concentration of 15% CO in the same column under identical conditions. It is seen that the enhancement effect of CO<sub>2</sub> on the separation of H<sub>2</sub>/CO is still present as for the total reflux operation. Further the values from total reflux operation seem to be in agreement with the plotted curves from the results of continuous operation. The 'maximum' effect in the separation due to the introduction of CO<sub>2</sub> is still present. The extent of the increase in the enrichment over that obtained in a straight binary separation, can be determined at any withdrawal rate. This increase in enrichment is reduced by an increase in the withdrawal rate, until at approximately 1,000 cc/min the separation of H<sub>2</sub>/CO is as for the binary mixture.

The design of columns for the continuous separation of a three component mixture, presents an even greater problem than for "total reflux" as it has been demonstrated in the present experimental work, and elsewhere by the authors [15]. The characteristic constants  $H$  and  $K$  are influenced by the withdrawal rate for a given mixture in a given system under steady state conditions. When the other effects associated with ternary mixtures are superimposed, the

problem would probably yield an extremely complex theoretical solution, and for design a more empirical approach is necessarily based on experimental pilot plant data from prototype thermal diffusion columns.

#### CONCLUSIONS

- (i) The existing and exact and approximate theoretical solutions for the separation by thermal diffusion of multicomponent mixtures do not apply to common gases.
- (ii) The transport equations developed for the separation of isotopes, whether binary or multicomponent mixtures, cannot be used for the design of vertical thermal diffusion columns as applied to the separation of common gases.
- (iii) It would appear that when considering the separation of ternary mixtures of common gases in vertical columns, the components do not act independently. There is a net effect governed by the extent of interaction between the molecules, and the particular physical characteristics of the mixture, such as density and viscosity.
- (iv) Experiments carried out both under total reflux and continuous operation, indicate an optimum concentration of a third component

for which the separation of the components of the mixture is a maximum. Further, the enhancement of the separation of the components concerned is a significant one. Refer-

ence has been made to the mixtures of  $H_2/CO/CO_2$ , and the uncertain state of the theory necessitates restricting the conclusions to these three gases.

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## The Graetz-Nusselt problem for a power-law non-newtonian fluid\*

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**Abstract**—The authors show how the Graetz-Nusselt problem in heat transfer theory may be extended to non-Newtonian flow. A simple rheological model, "the power law," is used to obtain a partial differential equation for the temperature profiles, to which a semi-analytical solution may be found. The temperature profiles are then used to calculate average outlet temperatures, as well as Nusselt numbers for several degrees of non-Newtonian behaviour. Tables are given for estimating the effect of non-Newtonian flow on the heating and cooling of fluids in tubes.

**Résumé**—Les auteurs montrent comment étendre le problème de GRAETZ-NUSSELT dans la théorie du transfert de chaleur à un fluide non newtonien. Un modèle rhéologique simplifié, désigné sous le nom de "loi de puissance" permet d'obtenir, pour la répartition des températures, une équation différentielle partielle, qui peut être résolue semi-analytiquement. Les répartitions des températures sont alors utilisées pour calculer une température de sortie moyenne ainsi que les nombres de NUSSELT pour différents écoulements non-newtoniens. Des tables permettent d'estimer l'effet d'écoulements non-newtoniens sur le réchauffage et le refroidissement de fluides circulant dans des tubes.

### 1. INTRODUCTION

THE solution to the following heat transfer problem was presented in 1885 by GRAETZ [5] and again in 1910 by NUSSELT [8]: A fluid flows with a fully developed laminar parabolic velocity profile in the  $+z$ -direction in a circular tube of radius  $R$ . In the region  $z < 0$  the fluid is at a uniform temperature  $T_1$ . At the section  $z = 0$  the fluid passes into a tube of the same radius, the walls of which are maintained at constant temperature  $T_0$ , greater or smaller than  $T_1$ , for all  $z > 0$ .

GRAETZ and NUSSELT obtained the temperature profiles  $T(r, z)$  in the flowing fluid by making the following assumptions: (1) steady state has been attained, (2) heat conduction in the  $z$ -direction is negligible in comparison with heat transport in the  $z$ -direction by the over-all fluid motion, (3) the equilibrium physical properties  $\rho'$  (density) and  $c$  (heat capacity per unit mass) are independent

of position, (4) the nonequilibrium properties  $\mu$  (viscosity) and  $k$  (thermal conductivity) are independent of position, (5) heat produced by viscous dissipation is neglected, (6) there are no external (body) forces acting on the fluid, and (7) the flow obeys NEWTON's laws of viscosity (which leads to the parabolic velocity profile). The calculations of GRAETZ and NUSSELT have been critically revised and extended by DREW [4] and by YAMAGATA [9].

This paper is concerned with the relaxation of the seventh assumption, so that a solution to the GRAETZ-NUSSELT problem for one non-Newtonian model is obtained. The non-Newtonian model chosen for the calculations is the "power-law," which has been proven useful for the description of pressure drops in flow systems, and for which some heat transfer calculations have already been made [1]. The flow of many plastics melts may be described in terms of this power law.

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## 2. ANALYTICAL STATEMENT OF THE PROBLEM

The steady flow of an incompressible fluid with no external forces is described by the set of three basic equations of continuity, motion, and energy [2]:

Continuity:

$$(\nabla \cdot \mathbf{v}) = 0 \quad (1)$$

Motion:

$$\rho'(\mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p - (\nabla \cdot \boldsymbol{\tau}) \quad (2)$$

Energy:

$$\rho'c(\mathbf{v} \cdot \nabla) T = -(\nabla \cdot \mathbf{q}) - (\boldsymbol{\tau} : \nabla \mathbf{v}) \quad (3)$$

in which  $\mathbf{v}$  is the local fluid velocity,  $p$  is the static pressure,  $T$  is the temperature,  $\mathbf{q}$  is the heat flux vector, and  $\boldsymbol{\tau}$  is the stress tensor. The term  $(\boldsymbol{\tau} : \nabla \mathbf{v})$  in the energy equation is the heat production due to viscous dissipation. The rôle of this term in Newtonian flow in tubes has been studied by BRINKMAN [3] and its importance in extrusion of molten plastics has been discussed by one of the authors [1]. Under normal conditions it is not important and is hence neglected in the remainder of this discussion.

For flow in cylindrical tubes the above equations may be simplified to:

Motion:

$$0 = -\frac{dp}{dz} - \frac{1}{r} \frac{d}{dr}(r\tau_{rz}) \quad (4)$$

Energy:

$$\rho'c v_z \frac{\partial T}{\partial z} = -\frac{1}{r} \frac{\partial}{\partial r}(rq_r) \quad (5)$$

in which  $\tau_{rz}$  is the shear stress in the  $z$ -direction per unit area on an element of fluid surface of constant  $r$ , and  $q_r$  is the heat flux in the radial direction  $r$ . In order to solve these equations we substitute for the fluxes  $\tau_{rz}$  and  $q_r$  the expressions:

'Power Law':

$$\tau_{rz} = -m \left| \frac{dv_z}{dr} \right|^{\frac{1}{n}-1} \frac{dv_z}{dr} \quad (6)$$

FOURIER'S Law:

$$q_r = -k \frac{\partial T}{\partial r} \quad (7)$$

in which  $m$  and  $n$  are constants in the empirical

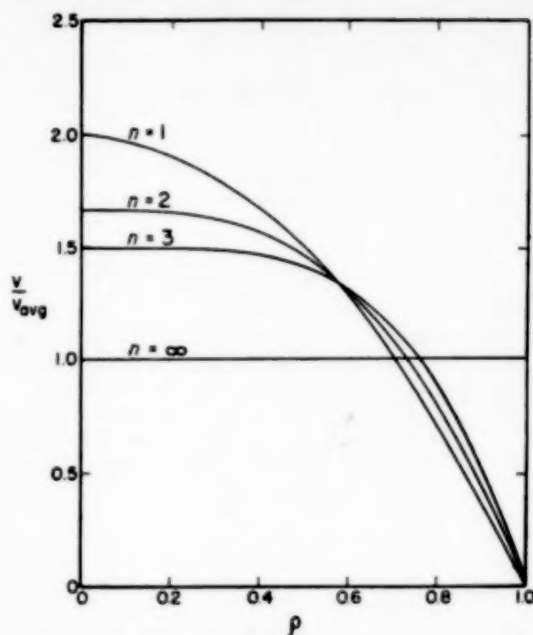


Fig. 1. Velocity distribution for the power law non-Newtonian fluids with  $n = 1, 2, 3, \infty$ .

modification of NEWTON'S law, obtainable from analysis of flow data in various types of viscosimeters [7],  $k$  is the coefficient of thermal con-

Table 1. The eigenvalues  $c_i$ .

$n$	1	2	3	$\infty$
$i$				
1	7.314	6.582	6.263	5.784
2	44.61	39.09	36.35	33.47
3	113.9	99.50	92.34	74.89
4	215.25	187.9	—	—

Table 2. The expansion coefficients  $B_i$ .

$n$	1	2	3	$\infty$
$i$				
1	1.476	1.493	1.516	1.602
2	0.806	0.850	0.866	1.065
3	0.589	0.643	0.634	0.851
4	0.476	—	—	—

Table 3. The Eigenfunctions  $\theta_i(\rho)$

$\rho$	$n = 1$			$n = 2$			$n = 3$			$n = \infty$		
	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_1$	$\phi_2$	$\phi_3$
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.982	0.892	0.735	0.988	0.884	0.766	0.984	0.911	0.782	0.986	0.925	0.821
0.2	0.929	0.605	0.153	0.935	0.646	0.288	0.938	0.668	0.269	0.943	0.718	0.380
0.3	0.846	0.234	-0.315	0.855	0.310	-0.257	0.854	0.335	-0.218	0.874	0.423	-0.095
0.4	0.738	-0.110	-0.392	0.756	-0.045	-0.403	0.765	-0.002	-0.404	0.782	0.106	-0.375
0.5	0.615	-0.342	-0.142	0.638	-0.311	-0.209	0.647	-0.264	-0.249	0.670	-0.168	-0.356
0.6	0.483	-0.432	0.170	0.506	-0.414	0.118	0.517	-0.399	0.062	0.543	-0.347	-0.113
0.7	0.351	-0.398	0.332	0.374	-0.385	0.310	0.380	-0.400	0.286	0.408	-0.403	0.166
0.8	0.224	-0.285	0.303	0.236	-0.293	0.310	0.245	-0.301	0.306	0.268	-0.339	0.299
0.9	0.107	-0.141	0.163	0.110	-0.166	0.185	0.117	-0.153	0.174	0.130	-0.188	0.218
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4 (a). Reduced temperature profiles  $\theta(\rho, \xi)$  for  $n = 1$ .

$\rho \backslash \xi \frac{v_{\max}}{v_{\text{avg}}}$	0.10	0.20	0.40	0.60	0.80	1.00	2.00
0.0	0.939	0.701	0.341	0.165	0.079	0.038	0.001
0.1	0.930	0.689	0.335	0.162	0.078	0.037	0.001
0.2	0.899	0.654	0.317	0.153	0.074	0.035	0.001
0.3	0.845	0.598	0.289	0.139	0.067	0.032	0.001
0.4	0.765	0.525	0.252	0.121	0.058	0.028	0.001
0.5	0.659	0.440	0.210	0.101	0.049	0.023	0.001
0.6	0.532	0.347	0.165	0.080	0.038	0.018	0.001
0.7	0.395	0.253	0.120	0.058	0.028	0.013	0.000
0.8	0.255	0.162	0.077	0.037	0.018	0.009	0.000
0.9	0.122	0.077	0.036	0.018	0.008	0.004	0.000
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4 (b). Reduced temperature profiles  $\theta(\rho, \zeta)$  for  $n = 2$ .

$\rho \backslash \zeta \frac{v_{\max}}{v_{\text{avg}}}$	0.10	0.20	0.40	0.60	0.80	1.00	2.00
0.0	0.926	0.670	0.808	0.140	0.063	0.029	0.001
0.1	0.923	0.663	0.804	0.138	0.063	0.028	0.001
0.2	0.888	0.629	0.288	0.131	0.059	0.027	0.001
0.3	0.884	0.577	0.263	0.119	0.054	0.025	0.001
0.4	0.764	0.513	0.233	0.106	0.048	0.022	0.000
0.5	0.667	0.435	0.196	0.890	0.040	0.018	0.000
0.6	0.543	0.346	0.156	0.071	0.032	0.015	0.000
0.7	0.408	0.256	0.115	0.052	0.024	0.011	0.000
0.8	0.262	0.162	0.073	0.033	0.015	0.007	0.000
0.9	0.124	0.076	0.034	0.015	0.007	0.003	0.000
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4 (c). Reduced temperature profiles  $\theta(\rho, \zeta)$  for  $n = 3$ .

$\rho \backslash \zeta \frac{v_{\max}}{v_{\text{avg}}}$	0.10	0.20	0.40	0.60	0.80	1.00	2.00
0.0	0.923	0.651	0.285	0.124	0.054	0.023	0.000
0.1	0.914	0.641	0.281	0.122	0.053	0.023	0.000
0.2	0.886	0.612	0.268	0.116	0.050	0.022	0.000
0.3	0.827	0.559	0.244	0.106	0.046	0.020	0.000
0.4	0.764	0.508	0.218	0.095	0.041	0.018	0.000
0.5	0.666	0.427	0.185	0.080	0.035	0.015	0.000
0.6	0.547	0.348	0.148	0.064	0.028	0.012	0.000
0.7	0.411	0.258	0.108	0.047	0.020	0.009	0.000
0.8	0.268	0.168	0.070	0.030	0.013	0.006	0.000
0.9	0.129	0.078	0.038	0.015	0.006	0.003	0.000
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000

ductivity. The use of this "power law" has been discussed in detail by REINER [7]. For Newtonian liquids  $m$  is the coefficient of viscosity  $\mu$  and  $n = 1$ .

Substitution of eq. (6) into eq. (4) gives an equation for the velocity distribution which may be integrated to give:

$$v_z = \frac{R^{n+1}}{m(n+1)} \left( -\frac{1}{2} \frac{dp}{dz} \right)^n \left( 1 - \frac{r}{R} \right)^{n+1}$$

$$= v_{\max} (1 - \rho)^{n+1} \quad (8) \quad \text{in which} \quad \theta = (T - T_0)/(T_1 - T_0) \quad \text{and}$$

in which  $\rho = r/R$  is the dimensionless radial variable, and  $v_{\max}$  is the maximum value of  $v_z$  at  $\rho = 0$ . The velocity profiles for  $n = 1, 2, 3$  and  $\infty$  are shown in Fig. 1. Substitution of FOURIER's law (eq. 7) and the velocity distribution (eq. 8) into eq. (5) then gives the partial differential equation for the temperature profiles:

$$(1 - \rho^{n+1}) \frac{\partial \theta}{\partial \zeta} = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial \theta}{\partial \rho} \right) \quad (9)$$

Table 4 (d). Reduced temperature profiles  $\theta(\rho, \zeta)$  for  $n = \infty$ .

$\rho \backslash \zeta \frac{v_{\max}}{v_{\text{avg}}}$	0.10	0.20	0.40	0.60	0.80	1.00	2.000
0.0	0.848	0.502	0.159	0.050	0.016	0.005	0.000
0.1	0.839	0.494	0.156	0.049	0.016	0.005	0.000
0.2	0.811	0.473	0.149	0.047	0.015	0.005	0.000
0.3	0.764	0.439	0.139	0.044	0.014	0.004	0.000
0.4	0.697	0.394	0.124	0.039	0.012	0.004	0.000
0.5	0.610	0.337	0.106	0.033	0.011	0.003	0.000
0.6	0.506	0.275	0.086	0.027	0.009	0.003	0.000
0.7	0.387	0.206	0.065	0.020	0.006	0.002	0.000
0.8	0.258	0.136	0.042	0.013	0.004	0.001	0.000
0.9	0.127	0.066	0.021	0.006	0.002	0.001	0.000
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 5. Average outlet temperature  $\theta_{\text{avg}}(\zeta)$ .

$n \backslash \zeta \frac{v_{\max}}{v_{\text{avg}}}$	1	2	3	$\infty$
0.1	0.579	0.558	0.541	0.394
0.2	0.395	0.370	0.351	0.216
0.4	0.190	0.168	0.152	0.069
0.6	0.091	0.076	0.066	0.021
0.8	0.044	0.035	0.029	0.007
1.0	0.021	0.016	0.012	0.002
2.0	0.001	0.000	0.000	0.000

Table 6. Nusselt numbers.

$n \backslash \zeta \frac{v_{\max}}{v_{\text{avg}}}$	1	2	3	$\infty$
0.1	4.21	4.42	4.59	6.06
0.2	3.03	3.15	3.25	3.92
0.4	2.03	2.08	2.12	2.33
0.6	1.52	1.54	1.56	1.63
0.8	1.20	1.21	1.21	1.24
1.0	0.98	0.98	0.99	1.00
2.0	0.50	0.50	0.50	0.50

$\zeta = (k/\rho'cv_{\max}R^2)z$ . Eq. (9) is to be solved for the boundary conditions:  $\theta = 1$  at  $\zeta = 0$ ;  $\theta = 0$  for  $\rho = 1$ ; and  $\partial\theta/\partial\rho = 0$  at  $\rho = 0$ .

### 3. SOLUTION FOR THE TEMPERATURE PROFILES

Equation (9) is solvable by the method of separation of variables, and the radial portion of the problem is of the Sturm-Liouville type. Hence the temperature profiles must be of the form:

$$\theta(\rho, \zeta) = \sum_{i=1}^{\infty} (-1)^{i+1} B_i \psi_i(\zeta) \phi_i(\rho) \quad (10)$$

in which the factor  $(-1)^{i+1}$  is included so that the tabulated  $B_i$  are positive. The  $\phi_i(\rho)$  are the eigenfunctions (orthogonal with respect to the weight function  $\rho(1 - \rho^{n+1})$  in the range  $\rho = 0$  to  $\rho = 1$ ) obtained from the solution of:

$$\frac{1}{\rho} \frac{d}{d\rho} \left( \rho \frac{d\phi_i}{d\rho} \right) + c_i (1 - \rho^{n+1}) \phi_i = 0 \quad (11)$$

the  $c_i$  being the eigenvalues. The  $\psi_i(\zeta)$  are

$$\psi_i(\zeta) = \exp - c_i \zeta \quad (12)$$

and the  $B_i$  are determined from the condition at  $\zeta = 0$  to be:

$$B_i = \frac{\int_0^1 \phi_i (1 - \rho^{n+1}) \rho d\rho}{\int_0^1 \phi_i^2 (1 - \rho^{n+1}) \rho d\rho} \quad (13)$$

Hence the problem is reduced to the determination of the eigenvalues  $c_i$  and the eigenfunctions  $\phi_i(\rho)$  for several values of  $n$  of interest. For  $n = 1$  the most extensive calculations are those of YAMAGATA [9], for  $n = 2$  calculations made earlier by one of the authors may be used [1], for  $n = 3$  new calculations [6] are reported here; for  $n = \infty$  (flat velocity profile) the  $\phi_i$  are just the zero-order Bessel functions  $J_0(\sqrt{c_i}\rho)$ . The  $\phi_i$  may be obtained as series solutions:

$$\phi_i(\rho) = \sum_{j=0}^{\infty} b_{i,j} \rho^j \quad (14)$$

in which the  $b_{i,0}$  are arbitrarily chosen to be unity and the higher coefficients are obtained from the recursion formula:

$$b_{i,j} = (c_i/j^2) (b_{i,j-n-3} - b_{i,j-2}) \quad (15)$$

The values of the  $c_i$  are obtained from eqs. (14) and (15) by use of the boundary condition at  $\rho = 1$  which requires that  $\sum_{j=0}^{\infty} b_{i,j} = 0$ .

The values of the  $c_i$  are given in Table 1, and the corresponding values of  $B_i$  may be found in Table 2. The eigenfunctions and reduced temperatures are presented in Tables 3 and 4 respectively. The tabulated values of  $c_i$  and  $B_i$  for  $i = 3$  and  $n = 2, 3$  are probably not so accurate as the number of figures would indicate, inasmuch as the accuracy was limited by the use of a 10-bank desk calculator. The tabulated values of the reduced temperatures are good to about 2%. Some sample temperature profiles are shown in Fig. 2. From the tables and graphs of reduced temperature profiles one may estimate the temperature distribution for the non-Newtonian fluid obeying the power-law model.

#### 4. AVERAGE OUTLET TEMPERATURE AND NUSSELT NUMBERS

For many problems the average outlet temperature of the fluid after passing through a length of pipe from  $z = 0$  to  $z = z$  may be desired. This temperature is defined by:

$$\theta_{avg} = \frac{T_{avg} - T_0}{T_1 - T_0} = \frac{\int_0^{2\pi} \int_0^1 \theta(\rho, \zeta) v(\rho) \rho d\rho d\phi}{\int_0^{2\pi} \int_0^1 v(\rho) \rho d\rho d\phi} \quad (16)$$

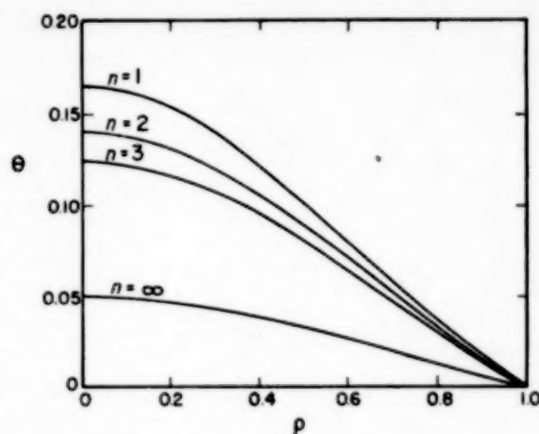


FIG. 2. Reduced temperature  $\theta(\rho, \zeta)$  for  $n = 1, 2, 3, \infty$  for  $\zeta(v_{max}/v_{avg}) = 0.6$ .

Values of  $\theta_{avg}$  are given in Table 5 as a function of the reduced length  $\zeta$  multiplied by  $(v_{max}/v_{avg})$ , which ratio has the values 2, 5/3, 3/2, 1 for  $n = 1, 2, 3, \infty$  respectively. This table allows a comparison of the reduced temperature change for fluid with the same thermal diffusivity and the same average velocity but with different degrees of deviation from NEWTON's law of viscosity.

The results may also be summarized in terms of the Nusselt number for heat transfer. First a heat transfer coefficient  $h$  is defined by the relation:

$$q = h \cdot 2\pi R z \cdot (T_1 - T_0) \quad (17)$$

in which  $q$  is the heat flow per unit time through the cylindrical surface of area  $2\pi R z$ . The heat flow through this surface must by an over-all energy balance be the same as the difference between the sensible heat input by flow at  $z = 0$  and the output at  $z = z$ . That is:

$$q = \pi R^2 \cdot v_{av} \cdot \rho' c \cdot (T_1 - T_{avg}(z)) \quad (18)$$

Combination of (17) and (18) along with the definition of the Nusselt number as  $Nu = 2Rh/k$  gives:

$$Nu = \frac{1 - \theta_{avg}(\zeta)}{\zeta v_{max}/v_{avg}} \quad (19)$$

The Nusselt numbers so calculated are shown in Table 6 for  $n = 1, 2, 3, \infty$ . The values of  $\theta_{avg}$



and  $Nu$  were obtained by numerical integration with Simpson's rule.

### 5. CONCLUDING REMARKS

The foregoing calculations represent only the first step in the study of heat conduction in non-Newtonian flow systems. Similar calculations need to be made for other non-Newtonian flow models (such as the Bingham plastic model, for example). Furthermore, the temperature dependence of the viscosity needs to be taken into account. Also, the tube-flow problem here discussed is but one of many geometrical arrangements which deserve attention.

At the present time it is not possible to make any comparisons with experimental data. There seem to be no data on heat transfer in laminar non-Newtonian flow, although such systems are of considerable industrial importance. There is also urgent need for experimental data on thermal conductivities and heat capacities of non-Newtonian fluids.

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### NOMENCLATURE

- $b_{i,j}$  = coefficients in (14)
- $c$  = heat capacity per unit mass
- $c_i$  = eigenvalues in (11)
- $k$  = coefficient of thermal conductivity
- $m, n$  = constants in power law model
- $p$  = static pressure
- $q$  = heat flow in (17)
- $q_r$  = heat flux, radial component (5, 7)
- $\mathbf{q}$  = heat flux vector
- $r$  = radial co-ordinate
- $\mathbf{v}$  = velocity vector
- $v_z$  = z-component of velocity
- $v_{avg}$  = average flow velocity
- $v_{max}$  = maximum flow velocity
- $z$  = axial co-ordinate
- $B_i$  = coefficients in (10)
- $Nu$  = Nusselt number in (19)
- $R$  = radius of tube
- $T$  = temperature
- $T_0$  = wall temperature
- $T_1$  = inlet temperature
- $T_{avg}$  = average exit temperature
- $\xi$  = dimensionless axial co-ordinate
- $\theta$  = dimensionless temperature
- $\theta_{avg}$  = dimensionless average exit temperature
- $\mu$  = Newtonian viscosity
- $\pi$  = 3.1416
- $\rho$  = dimensionless radial co-ordinate
- $\rho'$  = fluid density
- $\tau$  = shear stress tensor
- $\tau_{rz}$  = rz-component of shear stress tensor
- $\phi$  = polar co-ordinate
- $\phi_i$  = radial eigenfunction
- $\psi_i$  = solution to axial equation

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## Mass transfer between a flat surface and a falling liquid film

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**Abstract**—Measurements have been performed on the rate of solution of rather short surfaces of benzoic acid in a water film in laminar and turbulent flow. For the experimental conditions this process may be treated as the diffusion of solute from a plane surface into a laminar liquid flow with a constant velocity gradient. A reasonable agreement is found between the velocity gradients derived from the measurements and those which follow from otherwise known characteristics of falling films.

**Résumé**—On a mesuré la vitesse de dissolution dans un film d'eau, de plaquettes d'acide benzoïque. On a opéré dans les domaines d'écoulement laminaire et turbulent.

Dans les conditions expérimentales réalisées, ce problème peut être traité comme la diffusion d'un soluté à partir d'un plan à travers une couche laminaire à gradient de vitesse constant.

Les valeurs du gradient de vitesse calculées à partir de ces expériences sont en bon accord avec celles que l'on peut déduire des autres caractéristiques des films tombants.

### 1. INTRODUCTION

THIS study was undertaken because of interest in the resistance to heat or mass transfer across a liquid film flowing over a flat surface. In particular in the turbulent region such information might be of use for predicting the rate of heat transfer between a vapour and a cooled surface at high rates of the condensate flow. In principle, an experimental determination of the total resistance of the liquid film would require the establishment of a constant driving force over its two boundaries and the measurement of the resulting heat or mass flux at a point where the final temperature or concentration distribution has been reached.

In the present investigation a different approach to the experimental problem has been taken, and as a consequence, the information originally aimed at was not obtained. The experimental procedure was based on the assumption that the main resistance for transfer through a turbulent film would be located near the solid surface. This is not unreasonable since BRÖTZ [1] has shown with experiments on the spreading of dyes and on gas absorption in turbulent films that there exists a fairly high coefficient of mixing or "eddy diffu-

sivity" near the free surface. Thus, the experiments reported here had the purpose of determining the mass transfer rate between the solid surface and the bulk of the liquid film.

To this end a falling film of water was made on an inclined flat metal plate. At a downstream position, where the hydrodynamic flow was sufficiently established, a part of the plate was substituted by a soluble solid (benzoic acid) and its rate of dissolution was measured. The length of the soluble surface was varied between 5 and 80 mm. Now, owing to the small diffusivity of benzoic acid in water the depth of penetration of the solute into the liquid under these circumstances is so small that only the conditions in the laminar boundary layer are of influence on the rate of mass transfer. Thus these experiments only give information on the nonsteady diffusion into a laminar liquid flow with a constant velocity gradient and the further discussion will be restricted to this particular case. For obtaining data on the behaviour of the liquid beyond this boundary layer, much greater lengths of soluble substance would have been required. Experiments of this kind have recently been reported by STIRBA and HURT [2].

## 2. THEORY

The problem of heat penetration from a surface into the laminar boundary layer of established flow past the surface has already been solved by ELSE [3]. His result can equally well be used for the analogous case of diffusion. Since, however, ELSE's derivation is rather elaborate and a more elegant way of solving this problem exists, the latter will be given below.

The following problem, then, has to be solved. A flat plate of arbitrary breadth consists for  $x < 0$  of nonsoluble material and for  $x > 0$  of a substance with solubility  $c^*$  (Fig. 1). A liquid with solute concentration  $c = 0$  is flowing past the surface in the positive  $x$  direction. The flow is laminar and it has a constant velocity gradient  $dv/dy = a$  and a velocity  $v = 0$  at  $y = 0$ . The average rate of mass transfer is to be found between 0 and  $x$ .

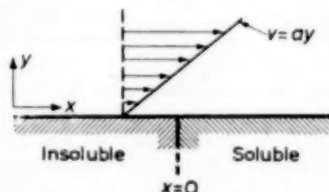


FIG. 1. Conditions for which eq. (1) is solved.

Neglecting the molecular diffusion in the direction of flow, we have the differential equation:

$$D \frac{\partial^2 c}{\partial y^2} - ay \frac{\partial c}{\partial x} = 0, \quad (1)$$

with the boundary conditions:

$$c = 0 \quad \text{for } x = 0 \text{ and } y \geq 0, \quad (2)$$

$$c = c^* \quad \text{for } x > 0 \text{ and } y = 0. \quad (3)$$

Equation (1) has a special solution of the source type:

$$c = S z^{-2/3} \exp(-y^3/z), \quad (4)$$

where

$$z = \frac{9D}{a} x.$$

$S$  is a constant which represents the source strength.

Solution (4) already obeys the boundary condition (2). By a superposition of infinitely small sources  $dS(\zeta)$  a general solution is obtained of the form:

$$c = \int_0^z e^{-y^3/(z-\zeta)} (z-\zeta)^{-2/3} dS(\zeta). \quad (5)$$

The function  $dS(\zeta)$  follows from boundary condition (3):

$$c^* = \int_0^z (z-\zeta)^{-2/3} \frac{dS}{d\zeta} d\zeta. \quad (6)$$

The latter equation yields:

$$\frac{dS}{d\zeta} = \frac{c^* \zeta^{-1/3}}{\Gamma\left(\frac{2}{3}\right) \Gamma\left(\frac{1}{3}\right)}. \quad (7)$$

Substitution of (7) into (5) gives for the concentration distribution:

$$c = \frac{c^*}{\Gamma\left(\frac{2}{3}\right) \Gamma\left(\frac{1}{3}\right)} \int_0^z e^{-y^3/(z-\zeta)} (z-\zeta)^{-2/3} \zeta^{-1/3} d\zeta. \quad (8)$$

Since we are interested in the rate of dissolution of the solid, the concentration gradient at  $y = 0$  has to be calculated from (8). This gives:

$$\left(\frac{\partial c}{\partial y}\right)_{y=0} = -\frac{3}{\Gamma\left(\frac{1}{3}\right)} c^* z^{-1/3}. \quad (9)$$

The value of the mass transfer coefficient,  $k$ , averaged over the distance  $x$  then becomes:

$$\begin{aligned} \bar{k} &= -\frac{D}{c^* x} \int_0^x \left(\frac{\partial c}{\partial y}\right)_{y=0} dx = \frac{9^{2/3}}{2 \Gamma\left(\frac{1}{3}\right)} \cdot \left(\frac{a D^2}{x}\right)^{1/3} \\ &= 0.808 \left(\frac{a D^2}{x}\right)^{1/3}. \end{aligned} \quad (10)$$

Exactly the same result can be derived from ELSE's solution of the problem.

A further development of the very general equation (10) depends on the hydrodynamic circumstances which indicate in what terms the velocity gradient  $a$  has to be expressed. For

gravity flow of a liquid film along a flat surface we have in the steady state :

$$\left(\frac{dv}{dy}\right)_{y=0} = a = \frac{g_x \delta}{\nu}, \quad (11)$$

where  $g_x$  is the component of the acceleration by gravity in the direction of flow  $x$ . The film thickness  $\delta$  may be expressed in terms of the liquid flow rate  $\Gamma_v$ . For laminar film flow we have the relationship :

$$\delta = \left(\frac{3 \Gamma_v \nu}{g_x}\right)^{1/3}. \quad (12)$$

This relation may also be written as :

$$\delta \left(\frac{g_x}{\nu^2}\right)^{1/3} = 0.909 \left(\frac{4 \Gamma_v}{\nu}\right)^{1/3}. \quad (12a)$$

According to many authors (12) or (12a) may be used up to  $Re =$  about 2,000, although already at low  $Re$  numbers rippling occurs and the velocity profile deviates from the theoretical one.

From experiments on turbulent films falling along a vertical wall Brötz [1] has shown that the film thickness may be described by the relationship :

$$\delta = 0.172 \left(\frac{\Gamma_v^2}{g_x}\right)^{1/3}, \quad \frac{4 \Gamma_v}{\nu} > 2360,^* \quad (13)$$

in which the viscosity no more occurs as a variable. Eq. (13) may also be written :

$$\delta \left(\frac{g_x}{\nu^2}\right)^{1/3} = 0.0683 \left(\frac{4 \Gamma_v}{\nu}\right)^{2/3}. \quad (13a)$$

Some controversy seems to exist in this field. DUKLER and BERGELIN [4] report that already at  $Re = 1,000$ ,  $\delta$  becomes greater than the value predicted by the laminar theory. However, JACKSON [5] recently showed that for a vertical water film eq. (12) applies at least up to  $Re = 4000$ . In view of these uncertainties the equation for the film thickness in laminar and turbulent flow along a flat plate will be written here :

$$\delta \left(\frac{g_x}{\nu^2}\right)^{1/3} = F \left(\frac{4 \Gamma_v}{\nu}\right) = F, \quad (14)$$

\* A similar result has been reported by KAMEI and OISHI [7].

where  $F$  is assumed to depend on  $Re$  only and not on the slope of the plate.

Substitution of (11) and (14) into equation (10) gives the final expression for the mass transfer coefficient  $\bar{k}$ , averaged over a distance  $x$ , between a flat surface and established laminar or turbulent film flow :

$$\bar{k} \left(\frac{\nu x^3}{g_x^2 D^3}\right)^{1/3} = 0.808 F^{1/3}. \quad (15)$$

For the experimental verification of this expression, it is essential that the penetration of solute does not extend beyond the region where the velocity gradient is constant.

#### 4. EXPERIMENTAL

The experiments were performed in a flat open duct which was 100 mm wide (Fig. 2). Its slope could be adjusted and for these measurements three values were chosen of the angle,  $\alpha$ , between the surface and a horizontal plane : 80, 45 and 6 degrees. At a distance of 330 mm downstream slabs of soluble material could be inserted in the manner indicated in Fig. 2. For these experiments benzoic acid was used and the slabs were cast separately, 100 mm wide and with variable length. Great care was taken that the slabs had a flat surface and that this surface could be fitted flush with the bottom of the duct. Before use the slabs were painted with a very thin layer of plastic paint (quick drying and smooth) except for a rectangular surface on the top side which was 80 mm wide and of which the length  $x$  was varied between 5 and 80 mm. The rate of dissolution of the slabs was measured at four different water flow rates which were measured with a calibrated rotameter.

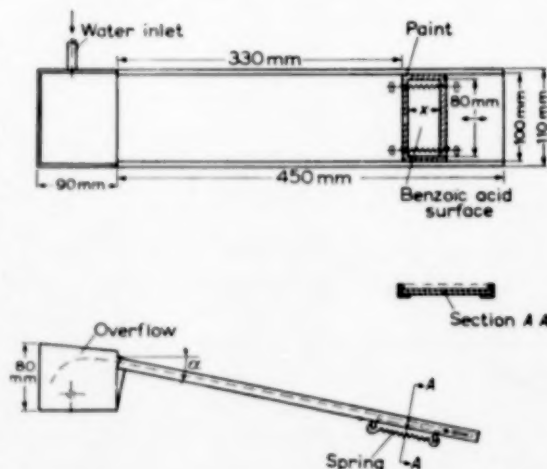


FIG. 2. Apparatus for the measurement of mass transfer to film flow.

The average mass transfer coefficient  $\bar{k}$  over the length  $x$ , was calculated with the formula

$$\bar{k} = \frac{\Delta M}{bx(c^* - c_{av})} \quad (16)$$

where  $bx$  = the area of the soluble surface and  $t$  = the time of exposure. The difference in mass  $\Delta M$  of the slabs before and after the experiment was obtained by weighing. Before weighing the slabs were dried during half an hour at 40°C. For the dissolution time a compromise had to be chosen. Too short a time would result in inaccurate  $\Delta M$  values and at too long times too much of the surface would be dissolved. According to circumstances  $t$  varied between 3 and 15 minutes. Since for the  $x$  values used the degree of saturation of the water was extremely small,  $c_{av}$  could be neglected with respect to the solubility of benzoic acid in water,  $c^*$ . The latter value, as well as the diffusivity of benzoic acid in water at the experiment's temperature, was taken from the paper by LANTON and SHERWOOD [6].

The experimental results have been collected in the Tables 1, 2, and 3 for  $\alpha = 80, 45$  and 6 degrees respectively. In the right-hand column the dimensionless group containing  $\bar{k}$  is shown. According to eq. (15) this group should depend on REYNOLDS's number only, so it should be constant for a series of experiments where  $\alpha$  and  $\Gamma_v$  are kept constant. For most combinations chosen this appears to be the case within a standard deviation  $\sigma$  of 5 to 10%. Only for  $\alpha = 80$  deg. and the two highest flow rates (Table 1) this group shows a significant trend as  $x$  is varied. From 14 duplicate runs (marked \* in Tables 1 and 2) it was found that  $\bar{k}$  had been measured with a standard deviation of about 8%.

As a summary of the results Table 4 shows the quantity  $F^{1/3}$  which was calculated from the mean values in Tables 1 to 3 according to eq. (15). Considering the standard deviations, there is no significant dependence of  $F^{1/3}$  on  $\alpha$ . There is, on the other hand, a significant correlation between  $F^{1/3}$  and REYNOLDS's number.

### 5. DISCUSSION

Since the accuracy of the experimental  $\bar{k}$ -values is not great and since  $\bar{k}$  does not strongly depend on the velocity gradient (compare eq. 10) it is hardly possible to use these measurements for predicting the thickness of falling films. On the other hand, it is of interest to compare the values found for  $F^{1/3}$  with those which can be deduced from the various existing correlations. Such a comparison is presented in Fig. 3. On the whole there is a fairly good agreement between the experimental values and those from the laminar theory ( $Re < 2,000$ ), and from the correlation (13) for turbulent flow. Still, one might want some explanation as to why the experimental values of

$F^{1/3}$  at  $Re \approx 3,500$  and 5,000 are low and those at  $Re \approx 7,000$  high.

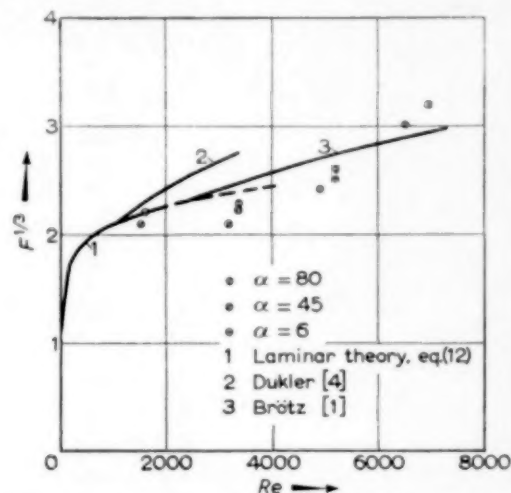


FIG. 3. Comparison between values of  $F^{1/3}$  (Table 4) and those derived from measurements of the film thickness.

Table 1. Mass transfer coefficients  $\bar{k}$ , for  $\alpha = 80^\circ$ ;  $T = 21^\circ\text{C}$ .

$\Gamma_v$ 10 <sup>-4</sup> m <sup>2</sup> /sec	$x$ 10 <sup>-3</sup> m	$\bar{k}$ 10 <sup>-5</sup> m/sec	$\bar{k} \left( \frac{\nu x^3}{g^2 D^6} \right)^{1/3}$	
17.1	80	4.78	3.13	
	60	5.00	2.97	
	40	5.65*	2.94	
	30	5.50*	2.60	
	20	6.13*	2.53	
	10	6.45*	2.12	mean = 2.57
	5	6.65	1.73	$\sigma = 0.46$
12.8	80	4.00	2.62	
	60	3.57*	2.22	
	40	4.14	2.15	
	30	4.23	2.00	
	20	4.90	2.02	
	10	5.30	1.74	mean = 2.06
	5	6.42*	1.67	$\sigma = 0.30$
8.3	80	2.96	1.94	
	60	3.20	1.90	
	40	3.66	1.91	
	30	3.89*	1.84	
	10	5.10	1.67	mean = 1.90
	5	8.25	2.14	$\sigma = 0.19$

Note:  $\bar{k}$  value marked \* is an average of two measurements



Table 2. Mass transfer coefficients  $\bar{k}$ , for  $\alpha = 45^\circ$ .

$\Gamma_v$ $10^{-4} \text{ m}^2/\text{sec}$	$T$ $^\circ\text{C}$	$x$ $10^{-3} \text{ m}$	$\bar{k}$ $10^{-3} \text{ m/sec}$	$\bar{k} \left( \frac{\nu x^3}{\epsilon_x^2 D^3} \right)^{1/3}$	
17.1	22	80	4.24*	2.94	
	15	40	3.47	2.22	
	23	40	4.76	2.56	
	15	30	3.54	2.06	
	22	30	4.68	2.34	
	15	20	4.48	2.27	
	23	20	6.12	2.63	
	15	10	5.73	2.30	
	23	10	6.45	2.20	
	15	5	7.01	2.25	
	23	5	8.62	2.35	
					mean = 2.37 $\sigma = 0.24$
12.8	15	80	2.27	1.83	
	22	80	3.18	2.20	
	22	60	3.34	2.08	
	15	40	3.07	1.96	
	23	40	3.29	1.76	
	15	30	3.40	1.98	
	22	30	4.00	1.99	
	15	20	3.80	1.93	
	23	20	5.25	2.24	
	15	10	4.70	1.89	
	23	10	5.15	1.75	
	15	5	5.87	1.88	
	23	5	8.02	2.16	mean = 1.97 $\sigma = 0.16$
8.3	15	80	2.22	1.79	
	22	80	2.45	1.53	
	22	60	2.78	1.58	
	15	40	2.79*	1.79	
	23	40	2.97	1.59	
	15	30	3.25	1.89	
	22	30	3.54	1.60	
	15	20	3.30*	1.67	
	23	20	4.24	1.81	
	15	10	4.90	1.96	
	23	10	4.63	1.56	
	15	5	5.24	1.68	
	23	5	6.10	1.64	mean = 1.70 $\sigma = 0.17$
3.9	14	80	2.24	1.85	
	22	80	2.56*	1.79	
	22	60	2.81	1.77	
	16	40	2.46	1.54	
	23	40	3.07	1.65	
	15	30	2.74*	1.59	
	22	30	3.27	1.63	
	15	20	3.74*	1.91	
	23	20	3.54	1.55	
	15	10	4.41*	1.78	
	23	10	4.83	1.64	
	15	5	5.28	1.69	
	23	5	6.37	1.71	mean = 1.70 $\sigma = 0.12$

Table 3. Mass transfer coefficients  $\bar{k}$ , for  $\alpha = 6^\circ$ ;  
 $T = 21^\circ\text{C}$ .

$\Gamma_v$ $10^{-4} \text{ m}^2/\text{sec}$	$x$ $10^{-3} \text{ m}$	$\bar{k}$ $10^{-5} \text{ m/sec}$	$\bar{k} \left( \frac{v x^3}{g x^2 D^3} \right)^{1/3}$	
12.8	80	2.16	2.34	
	60	2.11	2.07	
	40	2.32	2.00	
	20	2.86	1.96	
	10	3.47	1.87	mean = 2.04
	5	4.63	2.00	$\sigma = 0.15$
8.3	80	1.89	2.04	
	60	2.11	2.07	
	40	2.22	1.90	
	20	2.78	1.90	
	10	3.33	1.80	mean = 1.90
	5	3.94	1.69	$\sigma = 0.13$
3.9	80	1.65	1.79	
	60	1.98	1.94	
	40	2.05	1.76	
	20	2.47	1.69	
	10	3.28	1.78	mean = 1.79
	5	4.16	1.79	$\sigma = 0.08$

Table 4.  $\bar{F}^{1/3}$  calculated from experimental results.

$\frac{4\Gamma_v}{v}$	$\alpha$ deg.	$\bar{F}^{1/3}$
7000	80	$3.2 \pm 0.6$
6500	45	$3.0 \pm 0.4$
5200	80	$2.6 \pm 0.4$
4900	45	$2.4 \pm 0.2$
5200	6	$2.5 \pm 0.2$
3400	80	$2.3 \pm 0.2$
3200	45	$2.1 \pm 0.2$
3400	6	$2.25 \pm 0.15$
1500	45	$2.1 \pm 0.1$
1600	6	$2.2 \pm 0.1$

A reason for the observed discrepancy might be that under the experimental circumstances the entrance length of 0.33 m was too small for a sufficient establishment of the final flow pattern. This would result in too small  $\bar{F}^{1/3}$  values. It can

be shown that the characteristic length for establishing the final flow distribution is proportional to  $\Gamma_v^{2/3} g_x^{-1/3}$ . Thus the effect, if present, would be most pronounced at the higher  $Re$  numbers and a small value of  $\alpha$ . Since the results do not show such a discrimination, it is thought that this effect was of no great importance.

Too high values of  $\bar{k}$ , and thus of  $\bar{F}^{1/3}$ , might be obtained if the solute penetrates deeper into the liquid than the distance over which a laminar boundary layer with a constant velocity gradient exists. From eq. (5) it may be deduced that the depth of penetration is proportional to  $(Dx/a)^{1/3}$ . On the assumption of VON KÁRMÁN's velocity profile the distance over which the boundary layer is still laminar would be about  $5(v/a)^{1/2}$ . Thus at high values of  $x$  and  $a$  such an effect would be found first. This might partly explain the less satisfactory results presented in Table 1. Although in the measurements at high values of  $x$  reported there the solute may not have reached the limit of the "laminar" boundary layer, it is well possible that it has penetrated into that layer to such an extent that the diffusion is already increased by small eddies whereas the velocity gradient is still constant.

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#### NOTATION

$a = dv/dy$	( $\text{sec}^{-1}$ )
$c = \text{concentration}$	( $\text{kg m}^{-3}$ )
$D = \text{molecular diffusivity}$	( $\text{m}^2 \text{sec}^{-1}$ )
$F = \text{function of } Re, \text{ eq. (14)}$	
$g_x = \text{acceleration by gravity along } x (= g \sin \alpha)$	( $\text{m sec}^{-2}$ )
$k = \text{mass transfer coefficient}$	( $\text{m sec}^{-1}$ )
$T = \text{temperature}$	( $^\circ\text{C}$ )
$v = \text{velocity}$	( $\text{m sec}^{-1}$ )
$x = \text{coordinate in flow direction}$	( $\text{m}$ )
$y = \text{distance from wall}$	( $\text{m}$ )
$\alpha = \text{angle between } x\text{-direction and horizontal}$	(deg.)
$\Gamma = \text{gamma function}$	
$\Gamma_v = \text{volumetric flow rate}$	( $\text{m}^3 \text{sec}^{-1} \text{m}^{-1}$ )
$\delta = \text{film thickness}$	( $\text{m}$ )
$\nu = \text{kinematic viscosity}$	( $\text{m}^2 \text{sec}^{-1}$ )
$Re = 4\Gamma_v/\nu$	

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